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THE UNIVERSITY OF ALBERTA

OPTIMIZATION OF THE UNIQUAC PARAMETERS FOR AQUEOUS CARBOHYDRATE SOLUTIONS

by

KEN, KING YEE LUI

(C)

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR

THE DEGREE OF MASTER OF SCIENCE

IN

FOOD ENGINEERING

DEPARTMENT OF FOOD SCIENCE

EDMONTON, ALBERTA

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.....

Supervisor

.....

.....

Date: DEC 9, 1988

Dedicated to

- my beloved Parents

ABSTRACT

Previous studies have shown that the original UNIQUAC model fails to give an accurate representation of the thermodynamic properties of highly nonideal polar mixtures, particularly the water-containing systems. It has also been found that the model cannot in general represent the excess Gibbs energy and excess enthalpy simultaneously with satisfactory results. Previous modifications of the model only lead to moderate improvement.

Nevertheless, the successful application of the UNIQUAC model to aroma-water and sucrose-water solutions in our group suggests the capability of the model to describe the highly nonideal behavior of aqueous carbohydrate solutions. According to our studies, the problem in applying the model to aqueous carbohydrate solutions lies in the improper estimation of the structural parameters. In order to rectify the possible deficiencies of the original evaluation method, a new evaluation method is proposed and new parameter values for water and carbohydrate molecules are obtained. The validity of the new parameters is tested by applying them to several aqueous carbohydrate systems: xylose-water, glucose-water, fructose-water, sucrose-water and raffinose-water solutions. The resulting simultaneous representation of excess Gibbs energy and excess enthalpy of these systems is remarkably successful (%RMSD is well within 4%). With the new parameters the predictions of the freezing points and solubilities are shown to be in good agreement with the experimental values.

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LIST OF SYMBOLS

a_i	activity of component i
a_w	water activity
A_w	van der Waals surface area
a_{ij}	UNIQUAC adjustable binary energy parameter
c	a constant in equation [8.0-1]
D	objective function
G	Gibbs energy
H	enthalpy
K	equilibrium constant
$\bar{L}$	relative partial molar enthalpy
l_i	bulk factor of component i
M	molecular weight
m	molality
P	pressure
q	UNIQUAC surface parameter
Q_k	surface parameter of group k
r	UNIQUAC size parameter
R_k	size parameter of group k
R	universal gas constant
S	entropy
S^2	objective function
T	temperature in K
T_B	boiling temperature
T_F	freezing temperature

U	energy content
u_{ij}	UNIQUAC binary interaction parameter
V	volume
V^*	normalizing factor for R_k
V_w	van der Waals volume
x	mole fraction
Y_i	data point i for any measurement concerned
z	coordination number

Greek letters

γ	activity coefficient
Δ	change
θ	component surface area fraction
μ	chemical potential or partial molar Gibbs energy
υ	stoichiometric coefficient
π	osmotic pressure
τ	UNIQUAC energetic parameter
ϕ	osmotic coefficient
ϕ_i	component volume fraction

superscripts

E	excess
ID	ideal state
L	liquid state
M	mixing
•	pure state

°	standard state
∞	at infinite dilution
*	unsymmetric convention
–	partial molar quantity
(m)	molality standard state per kg solvent
(m)'	molality standard state per mole
(x)	mole fraction standard state

subscripts

i	component i
k	group k
r	response r
s	standard segment
1	solvent
2	solute
f	fusion
m	melting

Chapter 1 Introduction

One major concern of food engineering is the design of equipment and processes for efficient conversion of large quantities of raw materials into finished products. In the design and operation of such processes a large amount of reliable data on the equilibrium properties of materials are necessary. However, the limited availability of experimental data can hardly satisfy such an enormous demand. Engineers are thus required to rely primarily on a variety of methods for estimating physical properties of industrial interest.

Thermodynamics provides us with an efficient way to organize useful information from limited experimental measurements, and the prediction can be achieved by the use of a reliable and versatile thermodynamic model. Among various popular thermodynamic models, the UNIQUAC model has been shown to be a flexible and reliable model (Prausnitz et al., 1986; Eckert et al., 1980; Andersion and Prausnitz, 1978; Fredenslund et al., 1977; Abrams and Prausnitz, 1975), and has the potentiality to give an accurate thermodynamic representation of aqueous food solutions (Lee, 1987; LeMaguer, 1981 and 1985). Although the recent successful adaptation of the UNIQUAC model to represent the water-sucrose system (Lee, 1987) reveals the feasibility of further application of the model to other aqueous carbohydrate systems, previous studies (Zou and Prausnitz, 1987; Renon, 1985; Malanowski et al., 1981; Skjold-Jorgensen et al., 1980 and 1982; Eckert et al., 1980; Kikic et al., 1980; Anderson and Prausnitz, 1978) have shown that the original UNIQUAC model

fails to give an accurate representation of the thermodynamic properties of highly nonideal polar mixtures, particularly the water-containing systems, and the model cannot in general represent the excess Gibbs energy and excess enthalpy simultaneously with satisfactory results.

The modification introduced by Lee (1987) which gives significant improvement in the representation of the thermodynamic properties of aqueous sucrose solutions is, unfortunately, empirical; generalization of the modification to other systems is impossible. This study thus contributes to understand and identify the problems underlying, and based on the insight gained from these analyses a universal adaptation which is applicable to aqueous carbohydrate solutions is devised.

Chapter 2 Modelling of Aqueous Carbohydrate Solutions and the Food Industry

2.1 Aqueous Carbohydrate Solutions and the Food Industry

Man has been dealing with solutions since time immemorial. Without them it would be difficult to devise or organize any industrial enterprise. Among all these solutions, aqueous solutions are particularly important for the food industry as water is the most readily available solvent and is the single most important substance in food materials.

Water may occur as an intracellular and/or extracellular component in vegetables and animal products (deMan, 1982) and is found to be widely distributed throughout foods as a solvent system for sugars, salts, hydrophilic carbohydrates, gums, etc. (Zapsalis and Beck, 1985) Industrially, the use of water as a liquid base has at least two major advantages: a multitude of various processes can occur simultaneously within a relatively small volume (as compared to gas phase) of aqueous mixture, and water is able to retain and stabilize very complicated systems (e.g. living tissues) without limiting their mobility or interactive possibilities. In other words, the aqueous mixtures allow the creation of complex and multifunctional systems that are essential and useful for most food manufacturers.

Carbohydrates represent another major and important constituent of food. Despite the fact that carbohydrates contain only the elements carbon, hydrogen and oxygen, they occur in plant and animal tissues in many different

forms and at variable levels. Some important members in food include the sugars, dextrins, starches, cellulose, hemicelluloses, pectins and certain gums.

The large variety of carbohydrate constituents available to the food manufacturer offers a broad spectrum of properties when used individually or in combinations. These range from high to low with respect to sweetness, viscosity, consistency, solubility and many others. Furthermore, the proper manipulation of these properties by the variety of processes and techniques magnifies the multiple role which the carbohydrate constituents play.

As expected, solutions or mixtures formed by mixing various carbohydrates into water were found to exhibit useful physicochemical properties which allow widespread application in the food industry, for instance, they may function as sweeteners, as medium for fermentation, as preservatives, as osmotic agents, as thickening or gelatinizing agents, as stabilizers, as flavor retaining agents (Wienthes, 1968), etc. As a result, carbohydrates and water represent not only the two most abundant and important constituents of food materials, but also one of the most essential combinations in the food manufacturing industry.

2.2 Empirical Modelling of Aqueous Carbohydrate Solutions

Numerous studies on the physical and thermodynamic properties of aqueous carbohydrate solutions have been done. Nevertheless, the behavior of carbohydrates in solution is still not well understood. As there is at present no theory for predicting the properties of aqueous carbohydrate solutions with any degree of reliability, most effort has been devoted to developing empirical

correlations between measurable quantities and the desired function, e.g., the water activity.

Previous studies were mainly focused on the estimation or prediction of water activity. The importance of water activity in relation to food stability is well documented (Troller and Christian, 1978), and the effects of water activity on microbial growth, chemical reactions and enzyme activity have been studied extensively (Troller and Christian, 1978; Karel, 1975; Labuza, 1975;Scott, 1957).

A number of correlating equations for the calculation of water activity and activity coefficient of sugar solutions have been proposed in the literature. Those of Grover (1940) and Money and Born (1951), which were probably the best known in the confectionery industry (Norrish, 1966), and that of Dunning (1951), which is valid only for pure sucrose solutions, are all entirely empirical correlations. These equations are in many ways unsatisfactory because no significance can be attached to the values of the adjustable constants which appear in them and no confidence can be placed in their use outside the range over which they have been fitted to the experimental results. In addition, neither Gover's equation nor that of Money and Born is thermodynamically consistent in the sense that the Gibbs-Duhem equation cannot be satisfied without postulating absurd functional relationships between the activity coefficients of the solutes and concentration (Norrish, 1966). As a result, semi-empirical correlations were developed.

Based on the identity of equilibrium relative humidity (e.r.h.) with the thermodynamic activity, Norrish (1966) derived an equation for the activity

coefficient of water as a function of concentration in confectionery syrups. This thermodynamically based equation gives excellent accuracy with sugar solutions (Ross, 1975) and could be generalized to include multicomponent systems. However, it cannot be generalized to treat non-solute components (Ross, 1975). Based on the Gibbs-Duhem equation, Ross (1975) presented an equation for the prediction of water activity of aqueous solutions with the consideration of the non-solute materials, such as starches or proteins which bind water and help to lower water activity.

Modifications of these two semi-empirical methods of Norrish (1966) and Ross (1975) have been reported. Chuang and Toledo (1976) presented a modification of Norrish's equation, in which water activities of binary solutions were fitted as linear functions of the solute mole fraction. Ferro Fontan and Chirife (1981), and Ruegg and Blanc (1981) proposed modified Ross's equations. The water activity values of aqueous solutions and many liquid food systems have also been correlated to the thermodynamic expressions in terms of freezing point depression by many researchers (Ferro-Fontan and Chirife, 1981; Lerici et al., 1983; Chen, 1987 a,b). However, reliable freezing point depression data for solutions at high concentration are very limited.

All these shortcomings of the empirical or semi-empirical correlations indicate that there is no versatile model to give satisfactory prediction of water activity in complex aqueous solution. The attempt to apply thermodynamics in developing the correlations was crucial and critical but incomplete as the focus of most studies was on the water activity only. Such thermodynamic representation of a single component, water, in a complex system is not sufficient for most food operations. For the application of process modelling

techniques to food processes, a thermodynamic representation of each component in the system is necessary.

Chapter 3 Survey of the Current Models for the Excess Gibbs Energy

3.1 The Excess Gibbs Energy and Thermodynamic Modelling of Food Solutions

Thermodynamics is an efficient tool which allows us to extract the maximum amount of information with a minimum amount of experimental effort. As Prausnitz (1977) once pointed out, "Thermodynamics is not magic but a tool; it tells us how the desired equilibrium property is related to some other equilibrium property." In other words, thermodynamics provides us with a time-saving bookkeeping system; only a few equilibrium properties are needed to be measured, the rest can be calculated. Thus, from an engineer's point of view, the main advantage of thermodynamics is that it reduces experimental effort.

If thermodynamics is no more than an efficient tool for organizing useful information from limited observable measurements, the excess Gibbs energy will be no more than a useful quantity to achieve this goal. Because of the basic thermodynamic relationships which exist between the excess Gibbs energy and other useful parameters, the Gibbs function serves as an accounting function which allows us to quantify and characterize the deviation from ideality of the system (Prausnitz, 1969), and through it all other thermodynamic and physical properties of the system can be derived (as shown in Fig. 3-1).

Thus, the best way to approach the prediction of the behavior of complex solutions is through the use of the excess Gibbs energy function to represent thermodynamic properties (LeMaguer, 1987). Model expressed in excess

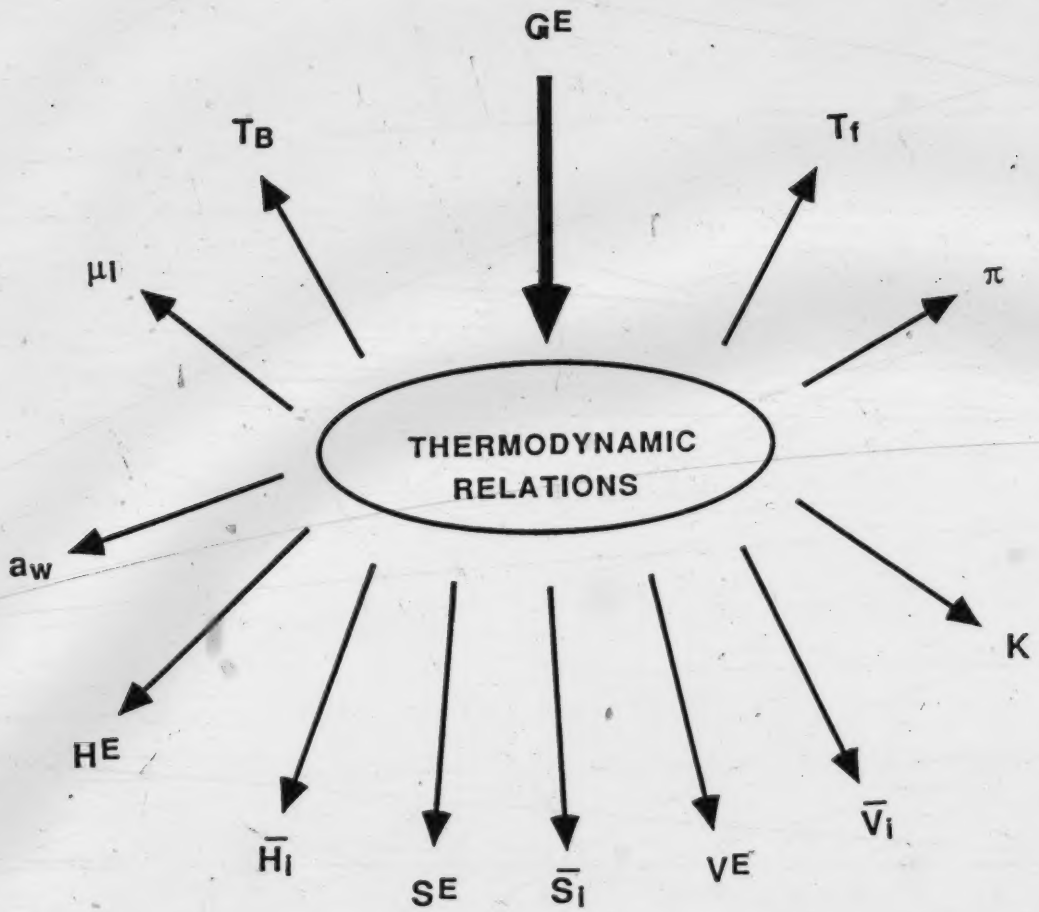

Fig. 3-1 The predictive power of the excess Gibbs energy

Gibbs energy can then be used to predict phase changes, water activity, activity coefficients of the solutes, and estimate partial equilibrium properties (LeMaguer, 1987).

Several attempts at applying some popular G^E models to food solutions have been reported. LeMaguer (1981) adapted the UNIQUAC model (Abrams and Prausnitz, 1975; Maurer and Prausnitz, 1978) to the system terpene-water with successful results. Lebert and Richon (1984) cited the work of Allaneau (1979), who used a number of non-electrolyte thermodynamic models to predict the infinite dilution activity coefficients of some aromatic compounds in solutions of olive oil from experimental data. LeMaguer (1985) applied equilibrium thermodynamics to describe the starch-water system. Sorrentino, Voilley and Richon (1986) used the ASOG (Derr and Deal, 1969) and the UNIFAC (Fredenslund et al.,1975) models to predict the infinite dilution activity coefficients of aroma compounds in water-carbohydrate and water-polyethylene glycol solutions at various concentrations. Choudhury and LeMaguer (1986) predicted the water activity in glucose solutions using the UNIFAC model (Fredenslund et al., 1975) with reasonable agreement between experimental and predicted values. Choudhury (1987) applied the UNIFAC model with a free-volume correction term (Oishi and Prausnitz, 1978) to glucose and other sugar solutions; slight improvements in prediction were found. Lee (1987) used the extended UNIQUAC equation (Christensen et al., 1983) to represent an aqueous solution of ethanol, sucrose and sodium chloride, with good results. From all these attempts, it is clear that models expressed in excess Gibbs energy do give a reasonable and complete description of the systems investigated. Apparently, the UNIQUAC model (Abrams and Prausnitz, 1975;

Maurer and Prausnitz, 1978) was capable of a good representation of complex aqueous food solutions with a minimum of adjustable parameters.

3.2 Empirical Representations of the Excess Gibbs Energy: Composition Dependence

Generally, mathematical representation provides a convenient method to reduce extensive tables of experimental data into a few equations and a means to transmit data from the experimentalist to the engineer. As a result, many empirical expressions have been proposed. Some popular expressions are those due to Margules, van Laar, Redlich-Kister, Scatchard-Hamer and Wohl. These empirical expressions share a common purpose: to describe the non-ideal behavior of the system investigated by fitting the experimental data through thermodynamically consistent correlations.

For a binary mixture, any expression for the excess Gibbs energy must obey the following 2 boundary conditions: $G^E = 0$ when $x_1 = 0$; $G^E = 0$ when $x_2 = 0$. The simplest polynomial expression satisfying these boundary conditions is $G^E = Ax_1x_2$, where A is an empirical parameter which is a complicated function of macroscopic and molecular properties, and is thus difficult to estimate *a priori* but has to be determined experimentally.

The equation obtained is called the two-suffix Margules equation. This simple expression, however, can only represent liquid mixtures containing constituents of similar size, shape and chemical nature (Sandler, 1977). More complex expressions are thus required for more complex mixtures.

One convenient extension would be: $G^E = x_1x_2 [A + B (x_1 - x_2) + C (x_1 - x_2)^2 + ...]$, where A,B,C are empirical parameters. This equation is commonly known as the Redlich-Kister expansion (Redlich and Kister, 1948).

The Redlich-Kister expansion provides a flexible algebraic expression for representing the excess Gibbs energy of a complex liquid mixture and gives an indication of the apparent complexity of the mixture (Prausnitz et al., 1986) as the number of terms retained depends on the complexity of the mixture, the accuracy of the experimental data, and the fit desired. Other similar expressions are the n-suffix Margules equations.

Another general expression is Wohl's expansion. Wohl (1946) developed expressions for the excess Gibbs energy involving weighted mole fractions (called q-fractions) and interaction terms up to a four-suffix (a_{hijk}) term. One of the main advantages of this method is that some rough physical significance can be assigned to the parameters which appear in the equations; as a result, Wohl's expansion can be extended systematically to multicomponent solutions.

All these equations share the common feature of expressing the relative frequency of a given kind of grouping, which is considered to be related to the contribution of a kind of interaction, in terms of the products of the effective mole fractions of the molecular species involved (Chao and Greenkorn, 1975). Implied in this expression is that the molecular collisions are random and that no modes are preferred. Chao and Greenkorn (1975) thus described these empirical equations as the Random-Solution equations to distinguish them from the equations which are based on the concept of nonrandomness.

Although the equations mentioned are frequently quite useful for correlating experimental data, or for making predictions (in a very limited sense) given a limited amount of experimental information, they are of little value in making predictions when no experimental data are available (Sandler, 1977). This is because their basis has been completely empirical, and little physical significance has been attributed to the parameters in these equations.

Furthermore, all random-solution equations are unable to predict multicomponent solution behavior from binary solution data alone. Multicomponent solution data are required for the evaluation of the higher interaction constants. This is rarely possible because of the scarcity of multicomponent solution data. But semi-empirical equations, like Wilson, NRTL, UNIQUAC, which are based on non-random binary interaction considerations, do not have this problem (Chao and Greenkorn, 1975). As a result, semi-empirical expressions based on sound theoretical arguments or concepts are found to be more versatile and powerful.

3.3 The Theory of Van Laar

A large number of semi-empirical models have been developed to explain the thermodynamic properties of binary mixtures on a quantitative basis for the past decades. One of the first systematic attempts to describe quantitatively the properties of fluid mixtures was made by van der Waals and his coworkers early in the twentieth century; however, significant contributions were due to van Laar, a student of van der Waals. Van Laar's work is still recognized today primarily because he chose good simplifying assumptions that made the problem solvable and yet did not greatly violate physical reality.

The theory of van Laar (1910,1913) is based on the assumptions that (1) the binary mixture is composed of two species of similar size and energies of interaction, and (2) the van der Waals equation of state applies both to the pure fluids and the binary mixture. The implication of assumption (1) is that the molecules of each species will be uniformly distributed throughtout the mixture and the intermolecular spacing will be quite similar to that in the pure fluids. Consequently, at a given temperature and pressure, $V^E = 0$ and $S^E = 0$ so that $G^E = U^E$. These simplifying assumptions allow the computation of U^E along the convenient path chosen by van Laar.

Despite the simplicity and elegance of the derivation of the van Laar equations, the equations are almost inapplicable to most real solutions, particularly polar nonideal mixtures. Quantitative agreement between van Laar's equations and the experimental data is not good. This poor agreement is mainly attributed to the use of the van der Waals equation of state and the mixing rules proposed by van der Waals (Acree, 1984), in addition to the simplifying assumptions.

3.4 Regular Solution Theory

Hildebrand (1929) first proposed "regular solution" to describe solutions which are characterized by the absence of any specific interactions between molecules, such as association, strong dipole interactions, and chemical effects, and in which the distributions and orientations are random (Hildebrand and Scott, 1962; Hildebrand et al., 1970).

The theory of regular solutions is, in fact, an extension of the van Laar equation. The extension leads to an expression of the equation constants in

terms of pure-component properties, thus making it possible to make estimates of slight and moderate departures from ideal-solution behavior from pure-component properties.

Because of the simplicity and generality of the regular solution equations, they are widely used for hydrocarbon solutions. If regular-solution calculations are compared with experimental vapor-liquid equilibrium data, the deviations have been found to be generally within reasonable bounds for hydrocarbon solutions (Chao and Greenkorn, 1975). Despite good results for the Gibbs energy of hydrocarbon solutions, the equations give poor results for the entropy and enthalpy. The fortunate results for the Gibbs energy are probably due to an apparent cancellation of errors in the entropy and enthalpy (Chao and Greenkorn, 1975). Furthermore, the extension of regular solution theory to multicomponent mixtures is an algebraically messy task (Sandler, 1977).

3.5 The Lattice Theory and Related Models

Most current work in the theory of solution utilizes the powerful methods of statistical mechanics which relate macroscopic (bulk) properties to microscopic (molecular) phenomena. Molecular considerations suggest that deviations from ideal behavior in liquid solutions are due primarily to the intermolecular forces (giving rise to a nonvanishing enthalpy of mixing), as well as the arrangements and orientations of unlike molecules in the mixture (giving rise to a nonideal entropy of mixing) (Prausnitz et al., 1986). As a result, recent models usually aim at describing the properties of solution in terms of intermolecular forces and fundamental liquid structure.

One popular approach to solution theory considers a liquid mixture as quasicrystalline (Guggenheim, 1952), i.e., to treat a liquid mixture as if the molecules were arranged on a lattice. In this the molecules do not translate fully in a chaotic manner as in a gas, but each molecule tends to stay in a small region, a more or less fixed position in space about which it vibrates back and forth (Prausnitz et al., 1986). In other words, we assume that molecules sit in a regular array in space (the lattice) and the motion of the molecules reduces merely to oscillations about some equilibrium positions. This is a rather questionable approximation for liquids. Hildebrand has already raised a number of arguments against the lattice model (Hildebrand and Scott, 1962). Nevertheless, a majority of investigators feel that the lattice model, though it may not truly represent the real liquid structure, gives the simplest way to a practical solution to the problem. Some facts may help to justify this "pro-lattice-theory" view: analysis by x-rays has shown that the mutual arrangement of neighboring molecules in liquids is much like that in a solid (Guggenheim, 1952; Prigogine, 1957); the available volume per particle in the liquid phase near the melting point is only slightly (about 10%) larger than in the solid (Prigogine, 1957); at temperatures well below the critical temperature, the number of nearest neighbors has a fairly well-defined average value and, although there are fluctuations about this average, these fluctuations are not large and the geometrical relationship of each molecule to its immediate neighbors is on the average very similar to that in a crystal (Guggenheim, 1952). But X-ray data on liquids also indicate that there exists in liquids only a local order but no long range order as in crystals (Eyring and Marchi, 1963). This signifies the main structural difference between a liquid and a solid crystal.

Using the concept of a quasicrystalline lattice as a model for liquid, Guggenheim (1935) devised an approximate treatment for regular solutions known as the quasi-chemical method. In this treatment, Guggenheim treated the molecules of the two components of a binary solution as spheres of approximately the same size with short range fields of force. Applying the methods of statistical mechanics, he predicted the general behavior of the thermodynamic functions for such a solution. A complete, detailed description and derivation of the method were presented in Guggenheim's monograph (1952).

When considering solutions containing molecules of differing sizes, it has been found advantageous to assume, at least as a first approximation, that the enthalpy of mixing is zero and to concentrate on the entropic contributions (Prausnitz et al., 1986). Solution having zero enthalpy of mixing are referred to as athermal solutions (Prigogine and Defay, 1954). Flory (1942) and Huggins (1941,1942) independently derived an expression for the entropy of mixing in an athermal solution containing molecules of different sizes by visualizing the molecules as occupying different numbers of contiguous sites in a liquid lattice. Flory and Huggins assumed a polymer molecule in solution behaves like a chain with a large number of equal sized segments identical in size to the solvent molecule. Each segment occupies a single site in the lattice and adjacent segments occupy adjacent sites. It was further assumed that a segment and a solvent molecule may replace one another in the liquid lattice. The total configurational entropy of the solution is then calculated by considering the arrangements of the molecules and their segments. The

derivation has been clearly presented in several references (for example: Flory, 1953; Fast, 1970).

Flory and Huggins developed a relatively simple counting procedure. However, the theory of Flory and Huggins implicitly assumed that the solution configuration is random, i.e., no preferential attractions occur between like or unlike species. This assumption is justified only if the polymer and monomer (including the solvent molecules) are similar in chemical nature. Expressions for the entropy of mixing have been derived by Orr (1944) and by Guggenheim (1944) which take into consideration the influence of preferential interactions.

To apply the theoretical result of Flory and Huggins to real polymer solutions it becomes necessary to add to the entropy computed a semi-empirical term for the enthalpy of mixing. The form of this term is the same as that used in the Scatchard-Hildebrand theory of solutions (or the regular solution theory); the excess enthalpy is set proportional to the volume of the solution and to the product of the volume fractions (Prausnitz et al., 1986).

The addition of an enthalpic term to the theoretical result is indeed an empirical modification required to obtain a reasonable expression for the Gibbs energy of mixing. Nevertheless, calorimetric studies indicate that the enthalpic term added does not properly describe the enthalpy of mixing of the solution (Prausnitz et al., 1986). Thus, though this relatively simple theory contains most of the essential features that distinguish solution of large molecules from those containing molecules of approximately equal sizes, the Flory-Huggins equation for real polymer solutions is not an accurate description of the thermodynamic properties of such systems.

3.6 Local Composition Models

The concept of local composition has been widely applied in the study of phase equilibrium for mixtures and used in the formulation of excess free energy equations. Important examples would be the Wilson equation (Wilson, 1964), the NRTL equation of Renon and Prausnitz (1968) and the UNIQUAC equation of Abrams and Prausnitz (1975).

The use of local composition is very appealing because it is an aspect of the structure of a liquid mixture that can be easily expressed in terms of intermolecular correlation functions and is thus amenable to statistical mechanical calculations (Seaton and Glandt, 1985). The following sections briefly review some successful local composition models and the underlying theories.

3.6.1 Local Composition Concept and the Wilson Equation

According to the molecular concept the random arrangement of the molecules in solution is more a postulate; indeed, it is more realistic to expect that the different sizes and forms of the molecules, as well as the stronger or weaker attractions acting between them or their segments, will interfere with their completely random arrangement. The quantitative description of such local inhomogeneity is achieved by the use of the local composition concept in which local mole fractions are defined. The concept is well illustrated by Cukor and Prausnitz (1969).

The introduction of the local composition concept has resulted in the development of many flexible and powerful models for excess Gibbs energy

(Rasmussen, 1983). Wilson (1964) obtained an expression for representing G^E by considering the preferential orientation of molecules due to energy effects. He postulated that the local concentrations in the neighborhood of a central molecule differ from the bulk concentrations because of the competition among the various molecular species in their interactions with the central molecule.

In the Wilson equation, the free energy of mixing is assumed to be given by a relation similar to the athermal Flory-Huggins equation, except that the overall solution volume fractions are replaced by local volume fractions which are related to local molecule segregations caused by differing energies of interaction between pairs of molecules. And the distribution of molecules about a central molecule is assumed to be expressible in terms of Boltzmann factors. Based on these two assumptions, the equation is derived (Wilson, 1964).

An important aspect of the Wilson equation is that only binary interactions are considered, and the equation constants, including all those in the equations for multicomponent mixtures, can be determined by fitting binary-solution data only (Chao and Greenkorn, 1975). However, the usefulness of the Wilson equation is limited to completely miscible systems (Prausnitz, 1969).

3.6.2 Two-Liquid Theory and the NRTL Equation

The two-liquid theory (or the two-fluid model) provides a useful point of departure for deriving local composition equations to represent thermodynamic excess functions for highly nonideal system (Prausnitz et al., 1986). The two-fluid model was devised independently by Scott (1956), by Byers Brown (1957) (who called it a semi-random approximation), and by Prigogine (1957) (who called it the "second refined version of the average potential model"). It was

introduced to allow for the departures of a real mixture from the randomness imposed by the one-fluid model.

The essence of the two-liquid theory lies on the assumption that there are two kinds of hypothetical fluids in a binary mixture: hypothetical fluid (1) has a molecule 1 at the center; hypothetical fluid (2) has a molecule 2 at the center. Each molecule is closely surrounded by other molecules. The excess free energy of the "two liquid" solution is then the sum of the free energy of transferring x_1 molecules 1 from pure liquid (1) to hypothetical fluid (1) in the solution and the free energy of transferring x_2 molecules 2 from pure liquid (2) to hypothetical fluid (2) in the solution. That is, the extensive configurational property of the mixture is considered to be the sum of contributions from the two hypothetical fluids (1) and (2).

Based on Scott's two-liquid theory, Renon and Prausnitz (1968) further developed Wilson's concept of local concentrations with the view of obtaining more universal expressions for liquid-phase activity coefficients. To define the local composition, Renon and Prausnitz made an assumption similar to that of the quasichemical theory of Guggenheim (1952). But unlike Wilson's model, the local composition is expressed in terms of mole fractions rather than volume fractions. Instead of using Flory-Huggins equation as in Wilson's model, Renon and Prausnitz used Scott's two-liquid theory of binary mixtures to obtain an expression for the excess Gibbs energy. The expression thus obtained is called the NRTL (nonrandom, two-liquid) equation.

One advantage that the NRTL equation offers over the Wilson equation is that the equation is applicable to partially miscible as well as completely

miscible systems. However, the NRTL equation contains three adjustable parameters for each binary system. This complicates the calculations, particularly when the equation is extended to multi-component system calculations.

3.6.3 The UNIQUAC Equation and Corresponding Models

In an attempt to develop a versatile model with fewer adjustable parameters, yet more theoretical basis, Abrams and Prausnitz (1975) used statistical mechanics to derive an expression for the excess Gibbs energy, called UNIQUAC (universal quasi-chemical). The UNIQUAC model generalizes the quasichemical lattice theory developed by Guggenheim (1952) and extends it to mixtures of molecules that differ appreciably in size and shape. As in the Wilson and NRTL equations, local concentrations are used. However, rather than local volume fractions or local mole fractions, UNIQUAC uses the local area fractions as the primary concentration variable. Then, in 1978, the model was rederived by Maurer and Prausnitz who used phenomenological arguments based on the two-liquid theory.

Because of its stronger theoretical base, the resulting equation which uses two adjustable parameters per binary is applicable to multicomponent mixtures of nonpolar and polar liquids. Theoretically, reliable estimates can be made of both vapor-liquid and liquid-liquid equilibria using the same equation for the excess Gibbs energy (Abrams and Prausnitz, 1975).

As compared to the previous local cornposition models, UNIQUAC has three advantages: (1) it has only two (rather than three) adjustable parameters; (2) because of its better theoretical basis, UNIQUAC's parameters often have a

smaller dependence on temperature; and (3) because the primary concentration variable is a surface fraction (rather than mole fraction), UNIQUAC is applicable to solutions containing small or large molecules, including polymers (Reid et al., 1977). All these are very important for engineering applications.

The flexibility and reliability of the UNIQUAC equation in the representation of both the vapor-liquid and liquid-liquid equilibria of a large member of binary systems, along with its straightforward extension to multicomponent systems, have prompted a number of researchers to attempt: (1) to transform UNIQUAC into group contribution models - Fredenslund et al. (1975, 1977) developed the UNIFAC model, a group contribution model based on the UNIQUAC method; (2) to apply UNIQUAC to electrolyte solutions - Christensen and coworkers (1983) proposed a model for aqueous electrolyte systems based on an extension of the UNIQUAC equation; (3) to apply the underlying concepts to derive similar expressions for G^E - Vera et al. (1977) proposed the Local Surface Guggenheim (LSG) and the Local Composition Guggenheim (LCG) equations which are quite similar to UNIQUAC and have no definite superiority over the UNIQUAC equation in terms of practical performance (Vera et al., 1977).

3.6.4 Applicability and Limitations of the Wilson, NRTL and UNIQUAC Equations to Nonideal Systems

Since the development of the local composition models, the applicability and performance of the Wilson, NRTL and UNIQUAC equations have been evaluated extensively. It can be demonstrated that, in weakly nonideal systems,

the differences between the individual equations for the dependence of G^E on the composition are very small and approach zero as the system approaches ideality (Novak et al., 1987; Reid et al., 1977). Thus, there is little reason to choose one over another for these systems.

A study of the Wilson equation by Orye and Prausnitz (1965) showed that for approximately 100 miscible binary mixtures of various chemical types, activity coefficients could be adequately described by the Wilson equation. The degree of precision is approximately the same as the four or five Redlich-Kister equations (Acree, 1984). However, there are two major limitations of the Wilson equation. First, the equation is not applicable to a mixture which exhibits a miscibility gap; it is inherently unable, even qualitatively, to account for phase splitting (Reid et al., 1977). Hence, it cannot predict liquid-liquid equilibrium. Unlike Wilson's equation, the NRTL and UNIQUAC equations are applicable to both vapor-liquid and liquid-liquid equilibria (Reid et al., 1977). Second, it is unable to predict maxima and minima in the activity coefficient - mole fraction relationship (Henley and Seader, 1981).

The accuracy of the three models (Wilson, NRTL and UNIQUAC) in phase equilibrium calculations has been studied. Monfort and Rojasr (1978) reported that vapor-liquid calculations for 34 binary systems and 9 ternary systems show a slight superiority of the UNIQUAC equation in the representation of experimental data.

As it has been mentioned, of the three solution models, only the NRTL and UNIQUAC models predict liquid-liquid equilibrium. In a series of investigations, Sorensen and his coworkers (1979a, b; 1980) evaluated the

NRTL and UNIQUAC equations with respect to their ability of representing binary and ternary liquid-liquid equilibrium data. They concluded that the UNIQUAC equation appears to be more convenient to use and to correlate the data slightly better than does NRTL with the same number of parameters. Monfort and Rojasr (1978) reported similar results in liquid-liquid calculations.

The capability of the three models to represent the excess enthalpy function has been investigated. As reported by Vonka et al. (1975) and Hanks et al. (1978) the Wilson equation cannot exceed certain positive values of H^E/RT, so that the H^E-fit is poor for systems showing strong endothermic behavior, while the UNIQUAC and NRTL equations are able to represent the experimental H^E data satisfactorily for those systems (Gmehling and Kolbe, 1983). For systems showing strong exothermic behavior, the H^E-representation is satisfactory for all three equations (Gmehling and Kolbe, 1983). According to Gmehling and Kolbe, for all the three models studied, the NRTL gives a better fit of the experimental data because of the presence of three adjustable parameters. The three parameters, however, are strongly correlated, so that several solutions are obtained depending on the initial values taken (Gmehing and Kolbe, 1983). Both the NRTL and UNIQUAC equations are able to describe different signs for different compositions.

In general, the UNIQUAC model can mathematically represent thermodynamic excess properties with a reasonable degree of accuracy and it has turned out to be a flexible and reliable model which allows satisfactory representation of vapor-liquid equilibria and liquid-liquid equilibria. Nevertheless, previous studies (Zou and Prausnitz, 1987; Brandani and Evangelista, 1984; Nath and Bender, 1981; Anderson and Prausnitz, 1978)

have shown that the original UNIQUAC model fails to give an accurate representation of the thermodynamic properties of highly nonideal polar mixtures, particularly the water-containing systems. It has also been found that the model cannot in general represent the excess Gibbs energy and excess enthalpy simultaneously with satisfactory results (Renon, 1985; Skjold-Jorgensen et al., 1980). Moreover, a precise simultaneous representation of VLE and LLE is not always possible (Skjold-Jorgensen et al., 1982; Malanowski et al., 1981).

3.6.5 Modifications of the UNIQUAC Equation

Attempts at improving the original UNIQUAC model have been reported. Anderson and Prausnitz (1978) introduced an extra empirical structural parameter q' in order to yield better results for those binary systems containing water or alcohols. The parameter q' is purely empirical and without any physical meaning. Improving the flexibility of a model by adding more parameters is dangerous since erroneous and erratic predictions of multicomponent behavior may result. To improve the simultaneous representation of excess Gibbs energy and excess enthalpy Skjold-Jorgensen and coworkers (1980) modified the UNIQUAC model by the introduction of a general temperature dependence of the coordination number. The modified UNIQUAC model is, however, better suited for the representation of mixtures containing non-associating components. It is probably necessary to include a special chemical term to properly describe system with association and solvation (Skjold-Jorgensen et al., 1980). Similarly, temperature dependent interaction parameters were introduced in order to represent the temperature dependence of the G^E function correctly (Nagata and Ohta, 1978). This

modification is merely based on a desired gain in flexibility. But practically, the improvement gained is completely outweighed by the increase in the number of model parameters (by a factor of 2) which makes the calculation as well as the determination of the model parameters difficult.

The combination of UNIQUAC with chemical theory is another attempt to improve simultaneous representation of VLE and LLE (Nagata and Kawamura, 1977). Nevertheless, the introduction of a chemical term does not sufficiently improve the representation (Skjold-Jorgensen et al., 1982). In addition, this leads to quite complicated expressions for the activity coefficients when more species are considered to associate or solvate.

Based on the assumption of concentration dependent interaction energies, Skjold-Jorgensen and coworkers (1982) presented a modification of the UNIQUAC model which takes into account solvation and association. Significant improvements in the simultaneous representation of VLE and LLE have been obtained due to the introduction of more fitting parameters into the model.

Extending the UNIQUAC model to associated solutions, Nagata and Kawamura (1979) first developed the UNIQUAC associated-solution theory to describe the excess properties of alcohols in unassociated active components. Nath and Bender (1981b) applied this association theory to alcohol, water and amine systems using pure-liquid association constants calculated from their molar enthalpies of vaporization at normal boiling point (Nath and Bender, 1981a). But Brandani and Evangelista (1984) showed that the UNIQUAC

associated-solution theory can be applied rigorously only for binary solutions containing one self-associating and one inert component.

Kikic et al. (1980) modified the combinatorial contribution to the excess Gibbs energy in the UNIQUAC equation. The prediction of the excess Gibbs energy of systems where the residual contribution may be expected to be zero (e.g., mixtures of aliphatic hydrocarbons) is found to be improved. The method, however, cannot be used for mixtures containing polymers.

Not one of these modifications significantly improves the performance of the UNIQUAC model. But these attempts do show the possibility of successful application of the model to various types of mixtures. And the number of modifications made to the original model further indicates the flexibility and adaptability of the model.

3.7 Thermodynamic Modelling of Aqueous Carbohydrate Solutions

The application of current popular local composition models to aqueous carbohydrate solutions is still recent (e.g., Choudhury and LeMaguer, 1986; Choudhury, 1987; Lee, 1987). Although the feasibility of the adaptation of the UNIQUAC model to aqueous sucrose solution has been demonstrated (Lee, 1987), further investigations are promptly required: to justify the selection of the UNIQUAC model, to identify and understand the problems found as UNIQUAC is applied to aqueous carbohydrate solutions, and finally, to rectify the identified problems by an appropriate scheme in order that the model can be applied more vigorously and extensively.

3.7.1 Model Selection: the UNIQUAC Model

As discussed in the previous sections, there are basically two types of equations which are commonly used for analytical treatment of the excess Gibbs energy function. The first group includes relationships correlating experimentally measured data without introducing generalizations. The parameters appearing in these equations are purely empirical and cannot be used for multicomponent systems. For instance, the Wohl's expansion involves a sequence of terms of increasing complexity representing interactions between larger and larger numbers of molecules. Each higher order interaction term in turn introduced one or more adjustable parameters the evaluation of which required experimental data of that order. That is, ternary interaction parameters require ternary data for their evaluation, etc. Thus, excess free energy models such as these are only correlative in nature, but not predictive. No generalization is possible. For engineering purposes, it will not be sufficient simply to reproduce the measured data. Engineers prefer general and versatile correlation allowing the evaluation of behavior over a wide range of variables (P, T, composition for multicomponent systems) of systems on which data are not available.

The second group consists of equations which are based on simplified molecular theory, that can be generalized and can, in principle, be used for multicomponent systems. For practical reasons, this group of equations is preferred due to their effectiveness and versatility.

Before evaluating the models in the second group, some thermodynamic properties of aqueous carbohydrate solutions are reviewed. Based on these observations, a sensible choice can be made.

Contemporary perspectives of carbohydrates define them as polyhydroxyaldehydes or ketones (Zapsalis and Beck, 1985). Because of this polyhydroxy nature, carbohydrate molecules usually have a high affinity for water molecules. This is demonstrated by the solubility of the low molecular weight carbohydrate molecules and the sorption of water by some polysaccharides. The mixture of water and soluble carbohydrate molecules is generally highly structured by the presence of numerous hydrogen bonds (Rowlinson, 1969). As a result, some local orderliness is expected in the mixture and the assumption of total randomness is unacceptable. This, indeed, justifies the use of local composition models to describe the thermodynamic behavior of aqueous carbohydrate solutions.

The thermodynamic behavior of aqueous solutions of some common sugars such as glucose and sucrose has been reported by a number of researchers (Taylor and Rowlinson, 1955; Stokes and Robinson, 1966; Scatchard et al., 1938; Robinson and Stokes, 1959 and 1961; Stroth and Schonert, 1977; Gucker et al., 1939; Garrod and Herrington, 1970; Honig, 1953). Recent systematic studies on the excess thermodynamic properties of aqueous solutions of mono- and oligosaccharides and their derivatives were carried out by Barone and his coworkers (1981a,b; 1982; 1983a,b,c; 1984; 1985; 1986). Based on these studies, some characteristic behavior of aqueous carbohydrate solutions can be outlined. All the data reported for the binary solutions show a slight but general positive deviations from Raoult's and

Henry's laws. The aqueous solutions of saccharides show a characteristic behavior in that the values of the excess functions (G^E, H^E and TS^E) are all positive. This behavior is quite different from that of the aqueous solutions of other hydrophilic solutes, such as the urea-like compounds (Barone et al., 1981c) or self-associating solutes, for which all values are negative. The positive values of the excess Gibbs energies are determined by the positive values of the excess enthalpies, that overwhelm the entropies. This fact suggests that the solute-solute interactions in aqueous solutions of monosaccharides are prevented or hidden by other more favorable interactions with the solvent. This is in agreement with spectroscopic and n.m.r. data (Franks, 1977; Walrafen, 1966). On the other hand, the structure of liquid water is stabilized by a series of specific interactions with the polar groups of the solute molecules. During the concentration process, the hydration is, however, partially retrogradated, the water molecules going back to the bulk state, richer in enthalpy and entropy. This retrogradation can account for the positive increasing values of H^E and TS^E. It is also found that, especially for the smaller solutes of the saccharide molecules, the enthalpic and entropic terms are comparatively large with respect to the excess Gibbs energy. The relatively lower values of G^E is due to the phenomenon called the enthalpy-entropy compensation effect (Lumry and Rajander, 1970). This may indicate that water plays the main role in determining the properties of these solutions. In addition, the values of G^E were found to relate with the number of equatorial OH groups of the carbohydrate molecules.

These findings indicate the highly nonideal and complex behavior of aqueous carbohydrate solutions and subsequently rule out the possibility of

applying some earlier solution theories and models such as the van Laar's model, the regular solution theory, the original lattice model, the Flory-Huggin's equation for polymer mixtures, to aqueous carbohydrate solutions due to the over-simplified assumptions used in their derivations.

Three models seem to offer considerable promise in their ability to represent such highly nonideal system and to be readily generalized to multicomponent systems. These are the Wilson equation (Wilson, 1964), the NRTL equation of Renon and Prausnitz (1968) and the UNIQUAC equation of Abrams and Prausnitz (1975).

Although the low molecular weight carbohydrate molecules are soluble in water, the solubility is limited. As the molecular weight of the molecule increases, the solubility decreases rapidly. The inability of the Wilson equation to represent heterogeneous systems severely restricts its application to aqueous carbohydrate systems.

Another major drawback of the Wilson equation is the incapability of fitting the higher values of heat of mixing (Hanks et al., 1978; Vonka et al., 1975). The aqueous solutions of saccharides have positive values of excess enthalpies, while the Wilson equation cannot exceed certain positive values of H^E. For the homogeneous systems with large positive deviations from the Raoult's law, which are in the vicinity of the heterogeneous region, Wilson equation leads to very low values of H^E. This fact cannot be eliminated even by introducing temperature dependent parameters (Vonka et al., 1975). These limitations are not found in the NRTL and UNIQUAC equations.

Although the NRTL equation is not restricted to one liquid phase system as is Wilson's equation, according to the analysis by Hanks et al. (1978), the NRTL equation suffers from a more serious limitation in the case of highly non-ideal solutions than does Wilson's equation because the G^E expression for the NRTL equation degenerates to an ideal solution model. Another main disadvantage of the NRTL equation is that it contains three adjustable parameters for each binary system. The values of the third parameter (described as a nonrandomness factor) are somewhat arbitrary and have little physical significance (Wang and Chao, 1983). The introduction of a purely empirical factor much weakens the theoretical soundness of the model.

Among the three, the UNIQUAC model is a more refined local composition model. It takes into consideration the influences of molecular sizes, shapes and energies of interaction on the distribution of species around a given molecules. Moreover, UNIQUAC has an advantage over NRTL, that is, it uses only two adjustable parameters per binary, instead of three.

Theoretically, the UNIQUAC model is not complete, but practically, it is useful and reliable. The recent successful adaptation of the UNIQUAC model for aqueous sucrose solution (Lee, 1987) may be a good indication of the feasibility of applying the model to other aqueous carbohydrate systems.

3.7.2 Problems and Limitations Encountered in the Applications of the UNIQUAC to Aqueous Carbohydrate Solutions

There has been no thorough investigation to correlate the thermodynamic behavior of the aqueous carbohydrate solutions using the UNIQUAC equation. One of the earliest attempts to apply the UNIQUAC

equation to describe the thermodynamic behavior of the sucrose-water system was attributed to Lee (1987). In order to understand the problems Lee encountered in applying the equation to aqueous sucrose solution, a brief summary of part of his study is presented.

In a preliminary study, Lee (1987) calculated the structural parameters (r_i & q_i) for sucrose and water molecules using the evaluation method suggested by Abrams and Prausnitz (1975). The UNIQUAC interaction parameters were optimized with the Simplex optimization method using experimental activity coefficients of water and sucrose at 25°C. The parameter optimization was based on the minimization of the weighted relative deviations of the activity coefficients (Lee,1987). It was found that good representation of the sucrose activity coefficient was obtained with this set of parameters. To test the validity of the parameters, Lee calculated the partial molar excess enthalpy of sucrose at 25°C by using the same set of parameters in the UNIQUAC calculations. The predicted values were found to be totally contradicted with the experimental data. From this observation, Lee concluded that the UNIQUAC equation can fit the excess Gibbs energy function properly but not the individual entropic and enthalpic contributions. Similar observations were made when Choudhury (1987) applied the UNIFAC model to aqueous glucose solutions. Indeed, these findings coincide with the study by Renon (1985) and Skjold-Jorgensen et al. (1980) when they applied UNIQUAC to other highly nonideal systems and concluded that the model cannot represent the excess Gibbs energy and excess enthalpy simultaneously. Fredenslund and Rasmussen (1985) pointed out that the proper representation of the total excess Gibbs energy results from fortuitous cancelling of the enthalpic and entropic contributions in this function.

To remedy this, Choudhury (1987) applied a free-volume correction (Oishi and Prausnitz, 1978) to account for the volume change in the solution which occurred upon mixing. However, this empirical modification does not significantly improve the performance of the model.

As the van der Waals parameters, used to estimate the r_i and q_i parameters in the UNIQUAC equation, are based on X-ray diffraction and microwave data of molecular crystals (Bondi, 1968), Lee (1987) argued that the r_i and q_i values of the sucrose molecule in solution should be different from those estimated from the crystal data. Instead of using a theoretical approach to recalculate the r_i and q_i values for sucrose molecule, Lee optimized the parameters by using the excess entropy data.

The optimized parameters were found to be significantly smaller than those calculated from the original evaluation method. Similar empirical findings were reported by Kikic et al. (1980) who proposed replacing the volume parameter r_i with $r_i^{2/3}$ in the UNIQUAC/UNIFAC equations.

Using the optimized parameters, Lee (1987) recalculated the excess entropy, excess enthalpy and activity coefficients of sucrose and water from the UNIQUAC equation. Good representations of all these functions were found. The average %RMSD is 6.6%. The new parameters also enable satisfactory prediction of the freezing point depression, boiling point elevation and sucrose solubility.

From these findings, one may conclude that the problem in applying the UNIQUAC equation to aqueous carbohydrate system lies in the improper estimation of the structural parameters, r_i and q_i.

Chapter 4 Analysis of the UNIQUAC Equation

The successful adaptation of the UNIQUAC model to represent the water-sucrose system (Lee, 1987) reveals the potential for application to other aqueous carbohydrate systems. Unfortunately, the modifications made by Lee were purely empirical; the new parameter values for sucrose were obtained by an optimization method. As these optimized parameters are valid only for the sucrose molecule, any generalization or extension is not possible. In other words, a new set of parameter values has to be re-determined for each carbohydrate molecule. This tedious process makes the previous adaptation inapplicable for general practical purposes. But before a universal adaptation, which is applicable to all carbohydrate molecules, is devised, a thorough analysis of the original UNIQUAC model and the problems inherent in the model is essential and critical.

Abrams and Prausnitz (1975) developed the UNIQUAC model from statistical mechanical arguments. A basic assumption in the model is that it is possible to define local mole fractions representative of the concentrations on a microscopic scale. These concentrations are different from the directly measurable overall mole fractions. But it has also been pointed out by Flemr (1976) and McDermott and Ashton (1977) that the expression has an inherent weakness because certain conservation equations are not satisfied. In 1978, Maurer and Prausnitz rederived the model using phenomenological arguments based on the two-liquid theory, thereby eliminating the inconsistency pointed

out by the previous authors. This settled the UNIQUAC model on a firmer theoretical foundation.

Some important features of the UNIQUAC model are as follows (Abrams and Prausnitz, 1975):

(1) The excess Gibbs energy is considered to be the sum of a combinatorial term and a residual term.

$$G^E = G^E_{(combinatorial)} + G^E_{(residual)}.$$

(2) $G^E_{(combinatorial)}$ is derived from Staverman's potential (Staverman, 1950), an extension of the Flory-Huggins athermal theory (Flory, 1941 and 1942) to molecules of differed shapes as well as sizes.

(3) $G^E_{(residual)}$ uses local area fraction as its concentration variable.

4.1 Combinatorial and Residual Contributions

4.1.1 Physical Significance and Differences of the two Contributions and their Relationship with the Excess Properties

The fundamental thermodynamic relation,

$$G^E = H^E - TS^E, \qquad [4.1\text{-}1]$$

considers the excess Gibbs energy as a combination of enthalpic (H^E) and entropic contributions ($-TS^E$). In this relation, the first term on the right is the manifestation of the energetic interaction between the molecules, while the second term is the measure of the order arising from the arrangement of the molecules in the mixture.

In the UNIQUAC model, a similar concept is employed: the equation for the excess Gibbs energy consists of additive terms that can be treated

separately. As a result, the excess Gibbs energy expression is separated into a combinatorial and a residual term:

$$G^E = G^E_{(combinatorial)} + G^E_{(residual)} \qquad [4.1\text{-}2]$$

Conceptually, the combinatorial term describes the dominant entropic contribution (Prausnitz et al., 1986). It involves the contribution due to the arrangement of multisegment molecules in the mixture, in the calculation of which all kinds of interactions between the molecules are left out of consideration (athermal concept). Under the assumption that each possible microstate is of identical energy, the combinatorial term can be evaluated by the use of statistical mechanics.

In a real mixture, the attractive-repulsive forces between the molecules or segments have to be taken into account. These forces displace the molecules from their initial arrangement, and make the presumed arrangement distorted. The residual term thus attempts to account for these energetic effects. It involves the contribution due primarily to intermolecular forces that are responsible for the enthalpy of mixing (Prausnitz et al., 1986).

Apparently, if one compares the equation [4.1-1] with [4.1-2] side by side, one would directly relate the combinatorial term to the excess entropy ($-TS^E$) and the residual term to the excess enthalpy (H^E). In order to assess the exactness of this statement and to explore the relationship between the two contributions of the UNIQUAC equation and the corresponding excess functions, the following transformations and comparisons are performed.

In the UNIQUAC equation,

$$G^E = G^E_{(combinatorial)} + G^E_{(residual)},$$

where

$$G^E_{(combinatorial)} = RT\left[\sum_i x_i \ln\frac{\phi_i}{x_i} + \frac{z}{2}\sum_i q_i x_i \ln\frac{\theta_i}{\phi_i}\right] \qquad [4.1\text{-}3]$$

$$G^E_{(residual)} = -RT\left[\sum_i q_i x_i \ln\left(\sum_j \theta_j \tau_{ji}\right)\right] \qquad [4.1\text{-}4]$$

where segment fraction ϕ_i , surface fraction θ_i, and the energetic parameters τ_{ji} are given by

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}$$

$$\tau_{ji} = \exp\left[\frac{-(u_{ji} - u_{ii})}{RT}\right] = \exp\left(\frac{-a_{ji}}{T}\right)$$

x_i is the mole fraction, z is the coordination number, r_i and q_i are the two structural parameters, a_{ji} is the adjustable binary energy parameter, and

$(u_{ji} - u_{ii})$ is the parameter representing the potential energy of interaction between molecules i and j.

By the Gibbs-Helmholtz equation,

$$\left[\frac{\partial\left(G^E/T\right)}{\partial T}\right]_{P,x} = \frac{-H^E}{T^2}$$

In the UNIQUAC equation, the parameters r_i and q_i are not temperature dependent. Assuming that the energy parameter a_{ji} is independent of temperature, we obtain

$$H^E = R\sum_i\left[\frac{q_i x_i}{\sum_j \theta_j \tau_{ji}}\left(\sum_j \theta_j \tau_{ji} a_{ji}\right)\right] \qquad [4.1\text{-}5]$$

Comparing equation [4.1-5] with [4.1-4], we find $G^E_{(residual)} \neq H^E$.

Since

$$-S^E = \left[\frac{\partial G^E}{\partial T}\right]_{p,x} \qquad \text{or} \qquad S^E = \frac{H^E - G^E}{T},$$

$$S^E = R\left[\frac{1}{T}\sum_i \frac{q_i x_i}{\sum_j \theta_j \tau_{ji}} \sum_j \theta_j \tau_{ji} a_{ji} - \sum_i x_i \ln \frac{\phi_i}{x_i} - \frac{z}{2}\sum_i q_i x_i \ln \frac{\theta_i}{\phi_i} + \sum_i q_i x_i \ln\left(\sum_j \theta_j \tau_{ji}\right)\right]$$

[4.1-6]

or

$$-TS^E = RT\left[\sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2}\sum_i q_i x_i \ln \frac{\theta_i}{\phi_i} - \sum_i q_i x_i \ln\left(\sum_j \theta_j \tau_{ji}\right) - \frac{1}{T}\sum_i \frac{q_i x_i}{\sum_j \theta_j \tau_{ji}} \sum_j \theta_j \tau_{ji} a_{ji}\right]$$

[4.1-7]

Comparing equation [4.1-7] with [4.1-3], we find $G^E_{(combinatorial)} \neq -TS^E$.

Therefore, it may be concluded that the two terms of the UNIQUAC equation are conceptually related to the H^E and TS^E functions but they are not exactly the same, because the combinatorial term only accounts for the athermal entropic contribution (i.e., $-TS^E_{(athermal)}$) and all the effects not included in the combinatorial term are taken into consideration in the residual term. In other words, the residual term, in fact, consists of the non-athermal entropic contribution as well as the enthalpic contribution. That is,

$$G^E_{(combinatorial)} = -TS^E_{(athermal)},$$

$$G^E_{(residual)} = -TS^E_{(non\text{-}athermal)} + H^E.$$

The combinatorial part is determined only by the composition and by the sizes and shapes of the molecules; it requires only the structural parameters, r_i and q_i. The residual part, however, requires also the energy parameters, a_{ji}. If the combinatorial term is directly related to the entropic function and residual term to the enthalpic function, the determination of the structural parameters as well as the energy parameters would be straightforward. Unfortunately, the relationship is found to be more complex. This complicates the determination of these parameters. As will be demonstrated in later chapters, the evaluation of the parameters from experimental measurements has to take this finding into consideration.

4.1.2 Entropic Contribution Related to Athermal Solution Concept: Influence of the Size and Shape of Molecules

The concept of athermal solutions has been developed by Flory (1942), Huggins (1942), and others in the study of polymer solutions. In the development of the UNIQUAC model, the athermal solution concept facilitates the formulation of the combinatorial term and thus enable the partition of the G^E expression into two parts: the combinatorial and the residual parts.

According to $G^E = H^E - TS^E$, the excess Gibbs energy consists of two parts, an excess enthalpy and an excess entropy. In an athermal mixture, the energy of mixing is assumed to be zero, i.e., $H^E = 0$, hence, $G^E = -TS^E$. This simplified assumption renders the consideration of molecular interactions unnecessary, and allows the formulation of the $G^E_{(combinatorial)}$ term by the use of statistical mechanical concepts of entropy.

In equation [4.1-3], the $G^E_{(combinatorial)}$ consists of two terms:

$$RT \sum_i x_i \ln \frac{\phi_i}{x_i} \quad \text{and} \quad RT \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i}$$

To reveal the physical meaning behind each of these two terms, a closer examination of the combinatorial contribution is presented as follows.

Let

$$G^E_{(comb1)} = RT \sum_i x_i \ln \frac{\phi_i}{x_i} \qquad [4.1\text{-}8]$$

and

$$G^E_{(comb2)} = RT \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i} \qquad [4.1\text{-}9]$$

For athermal mixtures, $G^E = -TS^E$, so

$$S^E_{(comb1)} = \frac{G^E_{(comb1)}}{T} = -R \sum_i x_i \ln \frac{\phi_i}{x_i} \qquad [4.1\text{-}10]$$

Since

$$\Delta S^{ID} = -\sum_i x_i \ln x_i \qquad [4.1\text{-}11]$$

thus

$$\Delta S^M_{(comb1)} = -R \sum_i x_i \ln \phi_i \qquad [4.1\text{-}12]$$

ϕ_i is the segment fraction; it measures the size of the molecule and thus directly relates with the volume fraction. If ϕ_i is replaced by the bulk volume fraction, equation [4.1-12] will become the Flory-Huggins entropy equation (Flory, 1942) which is derived for athermal mixtures of molecules of different sizes. This

indicates that $G^{E}_{(comb1)}$ is a term attempting to account for the size effect in an athermal mixture.

In a mixture of multisegment molecules consideration has to be given not only to the effect of the size of each multisegment molecule but also that contact occurs between the segments. If the molecule has r segments, and makes on average zq contacts, then the resulting nonideality may be taken into consideration by means of the surface fraction, θ_i, which is, in fact, a measure of the surface contact sites:

$$\theta_i = \frac{x_i\, q_i}{\sum_i x_i\, q_i} = \frac{x_i\, z\, q_i}{\sum_i x_i\, z\, q_i} \qquad [4.1\text{-}13]$$

Two molecules participate in a single contact; thus, the number of contacts per molecule is $zq_i/2$, and each contact contributes to the nonideality. The contribution of a single contact to the molar excess Gibbs energy is

$$RT \ln\frac{\theta_i}{\phi_i} \quad \text{(Guggenheim, 1952).} \qquad [4.1\text{-}14]$$

Thus the contribution of $zq_i/2$ contacts is

$$\frac{G^E}{RT} = \sum_i^{1/2zq_i} \ln\frac{\theta_i}{\phi_i} = \ln\left(\frac{\theta_i}{\phi_i}\right)^{\frac{1}{2}zq_i} = \frac{1}{2}\, zq_i \ln\frac{\theta_i}{\phi_i}$$

or

$$G^E = RT\frac{z}{2} q_i \ln\frac{\theta_i}{\phi_i} \qquad \text{(for molecule i)} \qquad [4.1\text{-}15]$$

For a multicomponent system,

$$G^E = RT\frac{z}{2} \sum_i x_i q_i \ln\frac{\theta_i}{\phi_i} = G^E_{(comb2)} \qquad [4.1\text{-}16]$$

That is, $G^E_{(comb2)}$ describes the surface (or shape) effect upon the combinatorial part, or more precisely, it accounts for the nonideality due to the neighbouring contact sites around each molecule. To summarize, it has just been shown that the first term of the combinatorial part describes the size effect while the second term describes the surface effect.

4.2 A Fundamental Deficiency: Evaluation of the Structural Parameters

There are two types of parameters in the UNIQUAC model, namely, the energetic parameters, a_{ij}, and the structural parameters, r_i and q_i. The energetic parameters are the adjustable parameters contained in the residual contribution. The best values of these adjustable parameters would be the optimized values determined from the experimental results. However, the structural parameters are non-adjustable and their values depend only on the molecular structures.

The results obtained by Lee (1987) indicated that the combinatorial part of the UNIQUAC equation was not properly evaluated. Since the combinatorial part is entirely determined by the structural parameters, the improper estimation of the structural parameters becomes the only possible cause. Lee's optimized

results on aqueous sucrose solutions have further shown that the original r and q were overestimated and that the "proper values" might be significantly smaller.

The improper estimation of the structural parameters has a pronounced effect on the representation of the excess functions. First, because of the adjustable nature of the energetic parameters, the improper evaluation of the structural parameters leads directly to incorrect estimation of the energetic parameters and, as a result, all parameters, both structural and energetic, are wrongly evaluated. Second, according to the analysis presented in Appendix G, the excess entropy function is largely determined by the structural parameters, while the excess enthalpy function is mainly determined by the energetic parameters. Therefore, incorrect structural parameters would directly result in improper representation of the excess entropy, and incorrect energetic parameters would give poor representation of the excess enthalpy function. This explains why both excess entropy and enthalpy were not properly represented in the previous studies (Choudhury, 1987; Lee, 1987), even though the excess Gibbs energy function was well fitted by optimization techniques. The proper representation of the excess Gibbs energy is in fact due to the fortuitous cancellation of the excess enthalpy and excess entropy (Fredenslund and Rasmussen, 1985).

4.2.1 Possible Deficiencies in the Assumption and Evaluation of the Structural Parameters

Previous attempts at modifying the structural parameters have been purely empirical. For instance, Lee (1987) used the experimental data to find

the optimum values of r_i and q_i for sucrose molecule; Kikic et al. (1980) introduced the exponent 2/3 to r_i, replacing r_i with $r_i^{2/3}$; Anderson and Prausnitz (1978) proposed an empirical surface parameter, q', in order to get better fit for systems containing water or alcohol molecules. Although these modifications may be satisfactory for correlation purposes, it is clearly a limitation where the aim is to improve a predictive model. It is desirable, therefore, to gain a better insight into the possible deficiencies of the existing predictive method.

The definition of the structural parameters r_i and q_i is the following: (Abrams and Prausnitz, 1975)

$$r_i = \frac{V_{wi}}{V_{ws}} \qquad [4.2\text{-}1]$$

$$q_i = \frac{A_{wi}}{A_{ws}} \qquad [4.2\text{-}2]$$

,where V_{wi} and A_{wi} are the van der Waals volume and surface area of molecule i, calculated from the work of Bondi (1968), and V_{ws} and A_{ws} the van der Waals volume and surface area of the standard segment. Abrams and Prausnitz (1975) selected a methylene group (CH_2) of a linear polyethylene molecule of infinite length as one standard segment. The volume and surface area of the standard segment, as calculated by Abrams from Bondi's value, are 15.17 $cm^3\ mol^{-1}$ and $2.5x10^9\ cm^2\ mol^{-1}$ respectively. Substituting these values into the defining equations of the structural parameters, we have

$$r_i = \frac{V_{wi}}{15.17} \qquad \text{and} \qquad q_i = \frac{A_{wi}}{2.5x10^9}$$

In this simple evaluation of the structural parameters, the first possible deficiency would be the choice of standard segment. The van der Waals values are normalized by means of the volume and surface area of a methylene group in polyethylene. This rather arbitrary choice of normalizing factors may not always be optimal as indicated by Skjold-Jorgensen et al. (1982).

The choice of a methylene segment as the standard segment is perfectly legitimate if hydrocarbon mixtures are concerned. It would also be a reasonable choice if it is a nonpolar organic mixture. But if the mixture is , for instance, a mixture of carbohydrate (a polyhydroxy compound) and water (a highly polar molecule), the choice would be unacceptable. In this case, a (CH-OH) group would probably a better choice than a (CH_2) group.

Although the normalization does not severely influence the calculation of the surface and segment fractions (θ_i and ϕ_i), equations [4.1-3] and [4.1-4] do indicate that the normalized surface area (q_i) enters into both the combinatorial and the residual parts of UNIQUAC as a factor of multiplication. As a result, the normalization has a significant influence on the calculation of the excess Gibbs energy. A proper choice of normalizing factors or standard segment is thus critical.

Secondly, the definition of the structural parameters assumes that r_i and q_i are independently determined from van der Waals volume and surface area. This contradicts the relation defining the bulk factor l_i (Abrams and Prausnitz, 1975);

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \qquad [4.2\text{-}3]$$

or $$zq_i = (z - 2)\, r_i + 2\,(1 - l_i)$$

This relation clearly indicates that r_i and q_i are related linearly. If r_i and q_i are determined independently, the bulk factor l_i will become an adjustable parameter without any physical significance. But, according to Guggenheim (1952) and Vera et al. (1977), l_i is not an adjustable parameter but should represent a structural condition of the molecule.

Thirdly, there has also been some arbitrariness associated with the selection of a value for z, the lattice coordination number. The z value represents the number of nearest neighbors in the lattice structure. According to Guggenheim (1952), the z value can vary from 6 to 12 depending on the type of packing. As indicated in equation[4.2-3], the variation of the z value does have some effect on the ratio of r and q. Table 4-1 showed the effect on (q/r) as z is varied.

Nevertheless, Rasmussen (1983) pointed out that the influence from variation in z in the combinatorial term is negligible. And Abrams and Prausnitz (1975) indicated that the numerical results for $\ln\gamma$ are insensitive to the choice of coordinate number z provided a reasonable value is chosen. Therefore, it has become common practice to set z equal to 10 and most researchers generally agree 10 is the best average value for most organic mixtures (Abrams and Prausnitz, 1975; Fredenslund et al., 1975; Bondi, 1968). In this study, we have consistently used z=10 and did not introduce any modification for this parameter because of the above justification.

Table 4-1: The r/q values for variation of z

assuming l = 1,

z	q/r = (z-2)/z *
6	0.67
8	0.75
10	0.80
12	0.83

* from equation [4.2-3]

4.2.2 Group Assignment Problem for Carbohydrate Molecules

According to Bondi (1968), the van der Waals volume and surface area of a molecule are found by summation of the corresponding group properties, that is,

$$V_{wi} = \sum_k \upsilon_k V_{wk} \qquad \text{and} \qquad A_{wi} = \sum_k \upsilon_k A_{wk}$$

,where k = 1,2,.....,N (number of groups in molecule i);

υ_k = number of groups of kind k in molecule i;

V_{wk}, A_{wk} = van der Waals volume and surface area of group k respectively;

V_{wi}, A_{wi} = van der Waals volume and surface area of molecule i respectively.

Since the structural parameters r_i and q_i are defined in terms of the van der Waals volume and surface area, similar additivity principle is applied to calculate r_i and q_i using corresponding group values (R_k and Q_k). That is,

$$r_i = \sum_k \upsilon_k R_k \qquad [4.2\text{-}4]$$

$$q_i = \sum_k \upsilon_k Q_k \qquad [4.2\text{-}5]$$

,where R_k and Q_k are the r and q values of group k respectively.

The fundamental assumption made in the above calculations is that a molecule is considered as an ensemble of identifiable structural units corresponding to the main chemical groups and the geometrical parameters (r and q) of the molecule is assessed from the volumes and surfaces of the individual groups using a simple additivity rule. This assumption is valid only when the defined functional groups are independent from one another, and these groups are able to give a realistic representation of the molecular structure. Hence, the validity of the assumption greatly relies on realistic group definition and appropriate group distinction. In the case of carbohydrate molecules, problems were found in both the group definition and group distinction. As a result, the existing functional groups are unable to give realistic representation of carbohydrate molecules.

The quality of the representation of a molecule depends on how the groups are identified. The UNIQUAC method adopted the "functional group" approach in which the basic groups are defined on a chemical basis, that is, the structural groups are taken as the chemical groups which might be expected on

a chemical basis to interact. Chemical reactivity becomes the major criteria to identify distinct groups existing in a molecule. Consequently, assemblies of atoms with identical chemical behavior, regardless of its position or geometrical relationship with other groups, will be considered as one distinct group.

A chemical basis may give an appropriate measure to define convenient chemical groups for interaction, but it does not give meaningful definition for structural units from which a geometrical property is estimated. For instance, on a chemical basis, a mannitol molecule has six OH groups. The six OH groups might chemically behave similar, but regarding the physical extent of the group, they should be different: the OH group at the end of the molecule has greater spatial extent than the one in the middle of the molecule. Hence, to distinguish this structural difference, it may be more sensible to represent the mannitol molecule by 2 (CH_2OH) and 4 (CHOH) groups than by 6 (OH), 2 (CH_2) and 4 (CH) groups.

For carbohydrate molecules, the definition and assignment of groups are further complicated by the presence of various isomers and the polyhydroxy nature of the molecules. In order to have a more realistic representation of carbohydrate molecules, these molecular characteristics have to be taken into consideration.

The existing functional groups are defined to be such fundamental units that no distinction can be made between groups of the same kind in different structural context. For instance, the contribution of a carbonyl group in a ketone (say acetone) is considered the same as that of a carbonyl group in an organic acid (say, acetic acid). Similarly, the contribution of a OH group in glucose is

considered the same as that in ethanol. This makes the evaluation necessarily approximate because the contribution of a given group in one molecule is not necessarily the same as that in another molecule.

Accuracy of representation improves with increasing distinction of groups; in considering, for example, mannitol, in a first approximation no distinction is made between the position (primary or secondary) of a hydroxyl group, but in the second approximation such distinction is desirable. This is particularly important for structurally complex molecules such as carbohydrates. The current "functional group" method does not provide sufficient distinct groups to give an accurate representation of the molecular structure of carbohydrates.

Chapter 5 Modified Evaluation Methods for the Structural Parameters

In view of the analysis presented in the last chapter, the most critical problem that confronts UNIQUAC is the evaluation of the structural parameters r and q. Quasi-lattice models assume the existence of a regular lattice. Each lattice site is occupied by an equal-sized segment of molecule i and is surrounded by z (the lattice coordination number) nearest neighbor sites. Each molecule i has r_i segments and zq_i nearest neighbor sites (or contact sites). Thus, a relation between zq_i and r_i can be obtained by direct counting. For a straight or branched open-chain molecule, Guggenheim (1952) showed that r_i is related to q_i by

$$\frac{1}{2} z (r_i - q_i) = r_i - 1 \qquad \text{(Guggenheim, 1952)}$$

or $$zq_i = r_i (z - 2) + 2 \qquad [5.0\text{-}1]$$

rearrange

$$zq_i = (r_i - 2)(z - 2) + 2 (z - 1) \qquad [5.0\text{-}2]$$

The first term on the right represents the total number of nearest neighbor sites for all internal segments, while the second term is the number of nearest neighbor sites of the two free-end segments.

In order to generalize equation [5.0-1] for more complex molecules, Abrams and Prausnitz (1975) defined a bulk factor l_i and introduced it into the Guggenheim relation.

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \qquad [5.0\text{-}3]$$

or $$zq_i = r_i(z - 2) + 2(1 - l_i) \qquad [5.0\text{-}4]$$

rearrange

$$zq_i = (r_i - 2)(z - 2) + 2[(z - 1) - l_i] \qquad [5.0\text{-}5]$$

According to equation [5.0-1] l_i is zero for straight or branched open-chain molecules. For compounds with rings the value of l_i should increase with one for each ring corresponding to the loss of one pair of contact points. Compare equation [5.0-5] with [5.0-2], it can be easily seen that the bulk factor, l_i, actually is a correction factor to account for the loss or gain of contact points due to "free-end" effect, i.e., contact points loss with free ends joined and vice versa. As the correction factor $2l_i$ represents the difference between the number of external contact points of an actual (bulky) molecule i and an open-chain molecule having the same r_i, $2l_i$ must be a whole number (or an integer).

With the usual methylene normalizing factor and z=10 some calculated values of l_i and their expected values are presented in table 5.1. It is seen that the calculated l_i values do not seem physically reasonable for all substances (Rasmussen, 1983).

Table 5-1 Calculated and expected values of the bulk factor l_i (adapted from Rasmussen, 1983).

Compound	Expected l_i	* Calculated l_i
Pentane	0	-0.278
Neopentane	0	-0.664
2,2,4-Trimethylpentane	0	-0.652
Cyclopentane	1	0.988
Benzene	1	1.751
Water	-	-2.32

* values are strictly calculated according to the original evaluation method suggested by Abrams and Prausnitz (1975).

Because of the theoretical inconsistency existing in the evaluation of the structural parameters, the UNIQUAC equation can only give an approximate description of the actual liquid behavior. This severely reduces the predictive potentiality of the model. It is, therefore, necessary to evaluate r_i and q_i in a consistent and unambiguous manner.

Vera et al. (1977) proposed an improved method for evaluating r and q, which eliminates most of the problems pointed out in the previous chapter. In 1985, Abusleme and Vera further extended the method to calculations in the group approach.

5.1 Vera's Approach

By combining Abram's defining equations for r_i and q_i (equations [4.2-1] and [4.2-2]) and Guggenheim's relation for r_i and q_i (equation [5.0-1]), Vera et al. (1977) obtained the following relation,

$$A_{wi} = \frac{(z-2)}{z}\frac{A_{ws}}{V_{ws}}V_{wi} + \frac{2A_{ws}}{z} \qquad [5.1\text{-}1]$$

,and showed that the above relation between A_{wi} and V_{wi} is in fact theoretically linear with a common slope for all families of compounds, but a unique intercept for each family. That is,

$$A_{wi} = k_1 V_{wi} + k_2 \qquad [5.1\text{-}2]$$

,where k_1 and k_2 are constants.

An explanation for this linearity, based on molecular considerations, has been given by Vera et al. (1977). By a least-square fit over forty-three of the more common open chain compounds, branched or unbranched (including alkanes, alcohols, aldehydes, ketones, nitriles, acids and esters), Vera et al. (1977) found that

$$k_1 = \frac{(z-2)}{z}\frac{A_{ws}}{V_{ws}} = 1.323 \times 10^8 \text{ cm}^{-1} \qquad [5.1\text{-}3]$$

and

$$k_2 = \frac{2A_{ws}}{z} = 6.259 \times 10^8 \text{ cm}^2 \text{ mol}^{-1} \qquad [5.1\text{-}4]$$

After combination of equations [4.2-2] and [5.1-2], and introduction of the above numerical values for k_1 and k_2,

$$zq_i = 0.4228\, V_{wi} + 2 \qquad [5.1\text{-}5]$$

Equation [5.1-5] can be generalized for molecules of any size and shape by

$$zq_i = 0.4228\, V_{wi} + 2\,(1 - l_i) \qquad [5.1\text{-}6]$$

Thus, the values of q_i can be evaluated without any particular assumption about the values of V_{ws} and A_{ws}.

Vera et al. (1977) also found that the van der Waals volume V_{wi} as calculated by Bondi (1968) is closely proportional to the liquid molar volume at 20°C. A least square fit over 33 compounds, including alkanes, alcohols, esters, ketones, alkylchlorides and aromatics, gives

$$V_{wi} = 0.554\, V_i^L\,(20°C) \qquad [5.1\text{-}7]$$

This gives an alternative to calculate V_{wi}. Equation [5.1-5] can be rewritten as

$$zq_i = 0.2342\, V_i^L\,(20°C) + 2\,(1 - l_i) \qquad [5.1\text{-}8]$$

On the other hand, for any assumed value of z, a value of A_{ws} can be obtained from equation [5.1-4] and then a value of V_{ws} from equation [5.1-3]. As a result, sets of self-consistent values of z, A_{ws} and V_{ws} are obtained which are reproduced in table 5-2. Conceptually, these new sets of normalizing factors (V_{ws} and A_{ws}) can be visualized as the van der Waals volume and surface area of an optimum arbitrary standard segment.

Table 5-2 Self-consistent sets of values of z, A_{ws} and V_{ws} (adapted from Vera et al., 1977).

z	A_{ws} (10^9 cm^2/mol)	V_{ws} (cm^3/mol)
6	1.88	9.46
8	2.50	14.19
10	3.13	18.92
12	3.76	23.65

From the above findings, a systematic scheme for evaluation of r_i and q_i which requires only the knowledge of the van der Waals volume V_{wi} and the bulk factor l_i can be outlined as follows.

1. Calculate V_{wi} either by Bondi's method (Bondi, 1968) or by equation [5.1-7] if the liquid molar volume at 20°C is known.

2. Assign l_i value according to the structural condition of molecule i. (Note: l_i is not an adjustable parameter. A discussion regarding numerical values for the bulk factor l_i has been presented by Vera et al., 1977.)

3. Find q_i by equation [5.1-6], or by equation [5.1-8] if the liquid molar volume at 20°C is known.

4. Find r_i by equation [4.2-1] with V_{ws} = 18.92 (assume z=10), or by equation [5.0-4].

In order to extend Vera's approach to group-contribution method, Abusleme and Vera (1985) defined

$$q_i = \sum_k \upsilon_k Q_k \qquad [5.1\text{-}9]$$

,where Q_k is the surface area parameter of group k.

And

$$zQ_k = 0.4228\, V_k + (2 - J_k) \qquad [5.1\text{-}10]$$

,where J_k is the number of groups bonded to group k in a molecule and V_k is the van der Waals volume of group k as given by Bondi (1968). In this version (Abusleme and Vera, 1985), the V_k values of the -O- group (ether) and the -OH group were modified empirically to produce better result.

Table 5-3 showed the calculated r and q values of some common carbohydrate molecules using Vera's method (Abusleme and Vera, 1985). Despite the structural differences exhibited by glucose and fructose molecules, the calculated r_i and q_i values for glucose are found to be the same as those for fructose. This clearly indicates that Vera's method is unable to differentiate isomers.

Table 5-3 Evaluation of r_i and q_i of some carbohydrate molecules by Vera's method (Abusleme and Vera, 1985)

Compound	V_{wi}	l_i	r_i	q_i
Xylose	65.94	1	3.49	2.79
Fructose	77.31	1	4.09	3.27
Glucose	77.31	1	4.09	3.27
Sucrose	155.67	2	8.23	6.38
Raffinose	234.03	3	12.37	9.49

5.2 The "Building Block" Method

5.2.1 Concept

Both structural and stereoisomers are commonly found in carbohydrates. These isomeric carbohydrate molecules exhibit diverse physical properties. It is therefore vital for any evaluation method to distinguish one isomer from the other. The inability of Vera's method to differentiate isomers, as shown in section 5.1, renders the method inapplicable to carbohydrate molecules.

Some concepts adopted in Vera's method are found inappropriate for isomers. Vera's approach is based on Guggenheim's relation for r and q which is, in fact, derived from a direct counting procedure with no consideration of any correction for structural modification occurring in isomeric molecules. The bulk factor l_i is introduced as a correction factor for structural complexity that affects this counting procedure. Generally, the use of bulk factor is adequate to indicate some global structural conditions, for instance, a linear chain, a branched chain, a ring, a series of ring, etc. However, it is unable to distinguish the local structural differences (i.e., different structures but with same molecular size and global structure). In Vera's method, exact physical meaning is attached to l_i that only allows the parameter to have limited possible values. As a result, l_i becomes an extremely insensitive parameter. In the case of carbohydrates in which isomers are common, the bulk factor becomes useless. It makes the evaluation of structural parameters of carbohydrate molecule to be necessarily approximate; precise estimation is virtually impossible.

Nevertheless, if the bulk factor is treated as an adjustable parameter, the physical meaning of the r and q relation will become obscured (a problem found in the original UNIQUAC method). The introduction of an extra adjustable parameter is undesirable.

The linearity between r and q assumed in Vera's method is only true for non-isomers but untrue for isomers. Isomers with equal number of segment r usually have different values of q.

As discussed in section 4.2.2, the accuracy of evaluation of the structural parameters depends on a realistic representation of the molecular structure. Vera's approach, however, inherited the group assignment problems that were found in the original evaluation method (see section 4.2.2). In order to improve the accuracy, a method with more realistic group definition and appropriate group distinction has to be developed. This may include increasing distinction of groups and definition of groups on a structural basis, rather than a chemical basis. The following is an attempt to find an optimal solution for carbohydrate molecules.

The central idea of the new method, termed the building block method, is to evaluate the structural parameters, r and q, by using a few simple basic structural units or building blocks which are able to give more realistic spatial representation of a molecular structure and have the capability to represent all carbohydrate molecules. The building blocks thus defined should be spatially unique and able to give more precise description of the spatial relationship between different structural units.

Some fundamental assumptions of the method are:

(1) a carbohydrate molecule in aqueous solution can be treated as an ensemble of identifiable structural units;

(2) the structural property of the molecule is the sum of the individual contributions of each structural unit in the molecule;

(3) a group defined on a structural basis is spatially unique.

5.2.2 Proposed Basic Structural Units for Carbohydrate Molecules

Carbohydrates are conveniently classified into three major groups: mono-, oligo-, and polysaccharides. Monosaccharides are the simplest carbohydrate units and are generally considered as the building blocks for oligo- or polysaccharides. Structurally, a monosaccharide unit can be considered as a carbon chain closed by an ether group (-O-) to form a ring on which hydroxyl groups are attached. The rings can be further linked together by some other ether groups to form a series of rings.

Despite the variable nature of carbohydrate molecules, only a few basic structural units are found repeatedly joined together if the molecule is divided segment by segment. These basic units can be classified into three categories: (1) the linkage unit, (2) the hydroxyl units and (3) the alkyl units. Only one kind of linkage unit is found, the ether group (-O-). The hydroxyl units form the backbone of the molecule; the (CHOH) group is the most common unit found in the ring, while the (CH_2OH) group is mostly found attached to the ring as a side group. A (COH) group may also exist as a segment of the ring structure in some carbohydrates such as fructose. Occasionally, some alkyl groups may be incorporated into the molecule. Table 5-4 summerizes the basic units found in

carbohydrate molecules. From this table, the glucose and fructose molecules can be represented as follows:

Glucose (or Glucopyranose) = 4 (CHOH) + (CH_2OH) + (CH) + (-O-)

Fructose (Fructofuranose) = 2 (CHOH) + 2 (CH_2OH) + (COH) + (CH) + (-O-)

Fructose (Fructopyranose) = 3 (CHOH) + (CH_2OH) + (COH) + (CH_2) + (-O-)

Table 5-4 Basic Structural Units for Carbohydrate Molecules

Type	Structural Unit	Comment
linkage	-O-	as link between rings or in a ring
hydroxyl	CH_2OH	
	HOH	essential backbone units
	COH	
Alkyl	CH_2	non-hydroxyl backbone units, exist
	CH	occasionally.
	C	

5.2.3 Estimation Methods for the R and Q Values of the New Structural Units

The r and q parameters play different roles in the UNIQUAC equation. Parameter r is a purely "size" factor which appears only in the combinatorial part of the UNIQUAC equation. Since the combinatorial part only accounts for the athermal entropic contribution, r is a pure-component structural parameter independent of all kinds of interactions between the molecules (athermal conditon). Thus, the physical significance of r is well defined and exact. However, the role q plays is much more complicated, mainly because q is a "surface" factor for both the combinatorial and residual contributions. In this case (non-athermal), the effect of molecular interactions on the actual value of q cannot be ignored. For weakly nonideal systems, it is still a good approximation to treat q as a pure-component structural parameter. But for highly nonideal systems, the environmental effect on q has to be considered. This is particularly significant for systems such as aqueous carbohydate solutions where polyhydroxyl compounds are dissolved in highly polar solvent.

Since r is a well defined parameter, the original definition of r by Abrams and Prausnitz (1975) is used to calculate the R values of the proposed structural units, and the r value of a molecule is then calculated by the group-contribution method.

$$R_k = \frac{V_{wk}}{V^*} \qquad [5.2\text{-}1]$$

and

$$r_i = \sum_k \upsilon_k R_k \qquad [5.2\text{-}2]$$

where k = 1,2,.....,N (number of groups in molecule i);

r_i, R_k = r values of molecule i and group k respectively;

V_{wk} = van der Waals volume of group k;

V^* = normalizing factor for R_k (or r_i)

υ_k = number of groups of kind k in molecule i.

With one exception, values of van der Waals volume given by Bondi (1968) — the current best estimate for van der Waals volume, are used to calculate V_{wk}. Bondi's value for the -O- group (ether) in an aliphatic chain is 3.7 $cm^3\ mol^{-1}$. Based on two studies by Kehiaian et al. (1971 and 1978), Abusleme and Vera (1985) confirmed that 10.23 $cm^3\ mol^{-1}$ is the best optimal value for the van der Waals volume of the -O- group. In this study, V_w (-O-) = 10.23 $cm^3\ mol^{-1}$ will be used in the calculation of R(-O-).

Instead of 15.17 $cm^3\ mol^{-1}$, the normalizing factor calculated by Abrams and Prausnitz (1975) using a methylene group as a standard segment, 18.92 $cm^3\ mol^{-1}$ is used for V^*. This is an optimal value calculated by Vera et al. (1977). Conceptually, V^* stands for the van der Waals volume of an optimum arbitrary standard segment.

The above analysis on the role of q clearly indicates that it is unrealistic to evaluate the q value of a molecule in a highly nonideal system using only the pure-component data. It is therefore inappropriate to apply the original definition of q (equation [4.2-2]) by Abrams and Prausnitz (1975) to evaluate the Q values of the new proposed structural units, with the exception of the alkyl

groups, since the original definition does not give a realistic measure of the surface effect denoted by q.

There is no easy way to account for all the factors that distort the surface of a molecule. Vera's approach, perhaps, is a get-around solution for simple molecule making use of the simple relation between r and q. However, for more complex molecules where the bulk factor is unable to indicate the actual complex structural condition, Vera's approach becomes ineffective. Hence, in order to obtain a more realistic q values which can represent the actual spatial surface effect, an optimization procedure is developed to seek the actual optimum Q values for the building blocks. The essence of the method is to calculate the Q values of the building blocks from the optimized q values of some representative molecules.

Because of the nonpolar nature of the alkyl groups, the Q values of these groups are simply calculated by the method proposed by Abusleme and Vera (1985), which has been shown to give the best estimates for nonpolar compounds.

For evaluation of Q values of the polar groups (the linkage and the hydroxyl units), optimization procedure is required to find the best values. This involves (1) the selection of structural homogeneous molecule which allows the determination of the Q value of a particular structural unit unambiguously, (2) the determination of the optimized q values of the selected molecules, and (3) the calculation of the Q values of the structural units from the optimized q according to the representation.

The structural homogeneity of a chosen molecule and the consideration of other representative homologs of that molecule would be the two important aspects that facilitate the selection of appropriate molecules used in the optimization procedure. A molecule is structurally homogeneous if it can be represented by a limited type of the proposed structural units. Ethylene glycol would be a perfect example as it can be represented by only one type of structural unit; ethylene glycol = 2 x (CH_2OH). This simple and homogeneous representation of ethylene glycol makes the calculation of the Q values of CH_2OH straightforward, i.e., Q(CH_2OH) = 1/2 q(ethylene glycol). The consideration of other representative homologs gives a better average and more universal Q value of a structural unit. It would be biased to evaluate the (CH_2OH) group from ethylene glycol alone, other polyols have to be considered.

In order to evaluate the Q values of the (CH_2OH), (CHOH), (COH) and (-O-) groups, three compounds from the polyol series and three from the sugar family were chosen. They are:

1. Ethylene Glycol = 2 (CH_2OH)
2. Glycerol = 2 (CH_2OH) + (CHOH)
3. Mannitol = 2 (CH_2OH) + 4 (CHOH)
4. Xylose = 4 (CHOH) + (-O-) + (CH_2)
5. Glucose = (CH_2OH) + 4 (CHOH) + (-O-) + (CH)
6. Fructose
   a). Fructofuranose = 2 (CH_2OH) + 2 (CHOH) + (COH) + (-O-) + (CH)
   b). Fructopyranose = (CH_2OH) + 3 (CHOH) + (COH) + (-O-) + (CH_2)

From the above representations, the following equations can be obtained:

$$q(\text{ethylene glycol}) = 2\,Q(CH_2OH) \qquad [5.2\text{-}3]$$

$$q(\text{glycerol}) = 2\,Q(CH_2OH) + Q(CHOH) \qquad [5.2\text{-}4]$$

$$q(\text{mannitol}) = 2\,Q(CH_2OH) + 4\,Q(CHOH) \qquad [5.2\text{-}5]$$

$$q(\text{xylose}) - Q(CH_2) = 4\,Q(CHOH) + Q(\text{-O-}) \qquad [5.2\text{-}6]$$

$$q(\text{glucose}) - Q(CH) = Q(CH_2OH) + 4\,Q(CHOH) + Q(\text{-O-}) \qquad [5.2\text{-}7]$$

$$q(\text{fructofuranose}) - Q(CH) = 2\,Q(CH_2OH) + 2\,Q(CHOH) + Q(COH) + Q(\text{-O-}) \qquad [5.2\text{-}8]$$

$$q(\text{fructopyranose}) - Q(CH_2) = Q(CH_2OH) + 3\,Q(CHOH) + Q\,(COH) + Q(\text{-O-}) \qquad [5.2\text{-}9]$$

,where q( ) is the q value of the molecule concerned and Q( ) is the Q value of the structural unit concerned.

The polyols are mainly selected to evaluate the Q values of the (CH_2OH) and the (CHOH) groups, while the sugar molecules are for the linkage group (-O-). Fructose is one of the few monosaccharides that contains the (COH) group. When fructose is dissolved in water, both the pyranose and furanose forms exist at equilibrium. According to Shallenberger (1982), there are 75% existing as fructopyranose and 25% as fructofuranose in aqueous fructose solution at 27°C. Thus, unlike glucose and xylose where over 99% exist as pyranose rings at room temperature, both the pyranose and furanose forms have to be considered in the calculations.

Since the ratio of the pyranose form of fructose to the furanose form is 0.75/0.25 at 27 °C (Shallenberger, 1982), equations [5.2-8] and [5.2-9] can be combined as follows:

$$0.25\,[\,2\,Q(CH_2OH) + 2\,Q(CHOH) + Q(COH) + Q(\text{-O-}) + Q(CH)\,] + 0.75\,[\,Q(CH_2OH) + 3\,Q(CHOH) + Q(COH) + Q(\text{-O-}) + Q(CH_2)\,] = q(\text{fructose}) \qquad [5.2\text{-}10]$$

or

$$1.25\,Q(CH_2OH) + 2.75\,Q(CHOH) + Q(COH) + Q(\text{-O-}) = q(\text{fructose}) - [Q(CH) + Q(CH_2)] \qquad [5.2\text{-}11]$$

Let

$x_1 = Q(CH_2OH)$,

$x_2 = Q(CHOH)$,

$x_3 = Q(COH)$,

$x_4 = Q(\text{-O-})$,

using the above equations [5.2-3] to [5.2-7] and [5.2-11], an overdetermined system is established, i.e.,

$$2\,x_1 = q(\text{ethylene glycol}) = b_1$$

$$2\,x_1 + x_2 = q(\text{glycerol}) = b_2$$

$$2\,x_1 + 4\,x_2 = q(\text{mannitol}) = b_3$$

$$4\,x_2 + x_4 = [q(\text{xylose}) - Q(CH_2)\,] = b_4$$

$$x_1 + 4x_2 + x_4 = [q(\text{glucose}) - Q(CH)] = b_5$$

$$1.25x_1 + 2.75x_2 + x_3 + x_4 = q(\text{fructose}) - [Q(CH) + Q(CH_2)] = b_6$$

This system of linear equations can be written as $A x = b$, where A is a coefficient matrix, b is a constant vector and x is the unknown vector.

$$\begin{bmatrix} 2 & 0 & 0 & 0 \\ 2 & 1 & 0 & 0 \\ 2 & 4 & 0 & 0 \\ 0 & 4 & 0 & 1 \\ 1 & 4 & 0 & 1 \\ 1.25 & 2.75 & 1 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6 \end{bmatrix} \qquad [5.2\text{-}12]$$

By knowing all the constants (the optimized q) in vector b, the unknown vector x (the Q values) can be solved numerically (the numerical method used will be discussed in chapter 7). Once all the Q values of the structural units are determined, the q values of any carbohydrate molecule can be calculated according to the molecular representation.

Chapter 6 Data Collection for Parameter Estimation

Unless a proper data block is supplied, an efficient and powerful optimization strategy for parameter estimation is useless. The validity of an estimate directly relies on a sensible collection of experimental data.

In this work, experimental data available from the literature are used. Since experimental data are hardly ever plentiful, section 6.1 describes an attempt to define the best possible data block that can be built from available experimental data from a practical point of view. The section is concluded by outlining the best available experimental data required to build the data block of the six selected aqueous systems. Section 6.2 describes the experimental effort to complete the data block of the water-glycerol system necessary for optimization.

6.1 Data Collection and Selection

Since q is a "surface" factor which is closely affected by molecular interactions, and the energy parameters, a_{12} and a_{21}, represent the characteristic energies arising from molecular interactions, binary experimental data are required to evaluate these parameters. A proper choice of the type of binary experimental data for optimization is essential.

In thermodynamics it is common practice to describe the deviation from ideal solution behavior by means of excess properties. As a result, experimental data on excess properties are available in the literature. Wisniak

and Tamir (1978) also pointed out that excess properties can provide data for evaluation of parameters characterizing interactions between unlike species in a mixture. It is thus evident that the excess functions would be an appropriate choice of data sources used to evaluate the optimum values of q_2, a_{12} and a_{21}.

Fundamentally, there are three basic excess thermodynamic quantities, namely, the excess enthalpy (H^E), the excess Gibbs energy (G^E) and the excess entropy (S^E). They are related by

$$G^E = H^E - TS^E. \qquad [6.1\text{-}1]$$

Hence, the determination of either two quantities would allow one to calculate the third one. Generally, calorimetric data such as the heat-of-mixing data, the enthalpy of dilution, the heat of solution, would directly lead to the determination of the excess enthalpy; activity coefficient data give the excess Gibbs energy.

Box and Draper (1965) have demonstrated that using multiresponse data for estimating the parameters in a model results in confidence regions for the parameters that are smaller than those obtained when the responses are considered individually. One response represents one independent set of measurements of a particular property of a system. For the excess functions, the excess Gibbs energy and the excess enthalpy would be two independent responses. In this study, all three excess quantities will be used to build the data block for the optimization procedure described in chapter 7. The following summarizes the best available experimental data for the evaluation of the excess functions of aqueous solutions of ethylene glycol, glycerol, mannitol, xylose, glucose, and fructose.

The thermodynamic properties of the binary system water-ethylene glycol have been extensively studied. A large collection of vapor/liquid equilibrium (VLE) measurements has been compiled by Gmehling and coworkers (1977 and 1981) in DECHEMA data collection. Almost all VLE measurements recorded in this data collection are isobaric T-x data, and there is only one set of isothermal P-x data at 80°C. Gonzalez and Van Ness (1983) reported another isothermal P-x data set at 50°C. A comprehensive heat-of-mixing data set at 25°C was reported by Touhara and Nakanishi (1979). More extensive heat-of-mixing measurements with temperature varies from 25 to 45°C were collected by Christensen and coworkers (1984). Additional sets of heat-of-mixing data at 50°C and isothermal P-x data at 60°C were reported by Villamanan, Gonzalez and Van Ness (1984) who reduced these data, together with other literature data, to provide correlations for H^E, G^E and S^E as functions of both composition and temperature. The correlations obtained were found to provide reliable values of the excess properties H^E, G^E and S^E for the binary system over a temperature range of 25 - 75°C and a concentration range (mole fraction) from 0 to 1; the calculated values from these correlations are in satisfactory agreement with values reported by Nath and Bender (1983). In this study, the correlations obtained by Villamanan et al. (1984) are used to generate experimental data from 25 to 75°C.

The water vapor pressure in water-glycerol system at 25°C has been studied in detail at low concentrations of glycerol by Scatchard, Hamer and Wood (1938) using the isopiestic method. The isopiestic data reported were found to be accurate and have been quoted and referenced by many other researchers (for example: Stokes and Robinson, 1966; Byron et al.,1978). The

region of high glycerol concentrations has been given detailed study by Kirgintsev and Luk'yanov (1962). The water vapor pressure measurements made by Kirgintsev and Luk'yanov were shown to be consistent with the data of Scatchard, Hamer and Wood. Since experimental activity data for the whole concentration range are required in this study, the two sets of measurements are pooled together. By use of a least-squares fitting technique, an empirical equation for the activity of water, $\ln \gamma_1$, is obtained. The activity of glycerol, $\ln \gamma_2$, can then be calculated by use of the Gibbs-Duhem equation. And, the excess Gibbs energy of this binary system is thus determined (see Appendix A).

The enthalpic measurements on aqueous solution of glycerol are surprisingly scarce. The International Critical Tables (National Research Council, 1929) has compiled a few enthalpic measurements made at the turn of this century. In 1953, Lange and Mohring reported the heat of solution of the water-glycerol system at 25°C; however, the measurements were made in very dilute solutions (concentration less than 0.25 molal). In view of having enthalpic data for the whole concentration range, the experimental data available from the literature is not sufficient. Therefore, more enthalpic measurements were made and the experimental details are described in section 6.2.

Enthalpy of dilution of aqueous solution of mannitol has been measured by Tasker and Wood (1982) as well as Stroth and Schonert (1977). Between these two sets of enthalpic measurements, the one by Tasker and Wood (1982) is chosen since statistical tests and error analysis have been performed and reported, which indicate that the measurements are consistent and have relatively low standard error (σ = 0.3 J/mol). The empirical expression obtained by Tasker and Wood also gives much lower relative error between the

experimental and corresponding calculated values as compared with the expression obtained by Stroth and Schonert which has more pronounced relative error, particularly serious in the dilute range.

Reliable and accurate isopiestic vapor pressure measurements for aqueous mannitol solutions were made by Robinson and Stokes (1961). The excess Gibbs energy function is calculated from the osmotic coefficients of mannitol reported (see Appendix D and E).

Although the pentose sugar, xylose, is not industrially important as glucose and fructose, sufficient experiment data on the excess properties of its aqueous solution can be found from the literature. Osmotic coefficients of xylose solution at 25°C were determined by Uedaira and Uedaira (1969) using the isopiestic vapor pressure method. These osmotic data permit the determination of the excess Gibbs energy function. Heats of dilution of xylose in water at 25°C have been measured calorimetrically by Barone and his coworkers (1981). The calorimetric data were then expressed in terms of excess enthalpy.

The thermodynamic properties of aqueous solution of glucose have been studied in detail by various researchers. Taylor and Rowlinson (1955) reported measurements of the vapor pressures of aqueous solutions of glucose from 25 - 65°C and up to a mole fraction of glucose of 0.195, the heat of dilution at 25°C up to a mole fraction of 0.245, and some other thermodynamic properties. Stokes and Robinson (1966) have presented a set of reliable osmotic data for aqueous glucose solution at 25°C. Savage and Wood (1976) determined the enthalpy of dilution of aqueous solution of glucose at 25°C in the more diluted

region (molality range: 0.18 - 2.0). Using these experimental results, Barone and his coworkers (1981) evaluated the excess functions of aqueous glucose solution at 25°C.

Finally, the enthalpy of dilution of fructose in water at 25°C has been determined calorimetrically by Barone et al. (1981), which was then expressed in terms of excess enthalpy. In 1986, Barone and his coworkers presented experimental result concerning the excess Gibbs energy at 25°C for the aqueous solution of fructose.

6.2 Calorimetric Measurements on the Glycerol-Water System — Isoperibolic Calorimetry

6.2.1 Experimental

Glycerol (ACS analytical grade, from BDH) was used as received. Minimum assay was 99.5% and impurity was less than 0.01%. It was stored in a vacuum desiccator before use. For all calculations in this experiment, glycerol was assumed 99.5% purity and contained no impurities other than water. All solutions were made up by weight using double distilled water and were used as soon after preparation as possible.

All calorimetric measurements have been made with an isoperibol calorimeter which has been described along with the operation procedure (Dobrogowska and Hepler, manuscript in preparation; Smith, 1988; see Appendix B). The calorimeter was immersed in a constant temperature bath maintained at 25.00 ± 0.01 °C and held constant during each calorimetric measurement to ±0.001 °C, using a temperature controller with an auxiliary

cooling system maintained at 24.80 ± 0.05 °C. Temperature changes in the calorimeter were measured with a thermistor combined with a Current Comparator Resistance Bridge (Guildline 9975).

Aqueous glycerol solution with predetermined concentration was weighed into the glass Dewar vessel. The mixture was stirred continuously and the change in resistance of the thermistor with time was recorded. When the resistance of the thermistor reached a value (3006.60 ohms) that had been shown previously to correspond to the temperature of the water bath, a known volume of water in the titrator was admitted to the Dewar vessel. The titration led to a change in temperature of the mixture and a corresponding change in resistance of the thermistor. The change in resistance of the thermistor with time was recorded. The calorimeter was then calibrated electrically.

The resistance changes due to the titration and the electrical calibration are calculated by standard methods (Vanderzee, 1981). Since the ratio of the resistance changes is equal to the ratio of the energy changes associated with the two processes, the energy associated with the titration can be calculated by knowing the electrical energy of the calibration (see Appendix B).

The accuracy and precision of the calorimetric system have been checked by the measurement of the enthalpy of solution of $KCl_{(c)}$ in distilled water. Result of the measurement, as fully reported elsewhere (Dobrogowska and Hepler, manuscript in preparation), agree to within 0.5% (accuracy) with the "best" values from the literature. The precision was found to be 1.2%. In the case of the water/glycerol system, larger uncertainties are expected as glycerol is highly hygroscopic.

6.2.2 Results and Discussion

Heats of solution of small quantities of pure water in large quantities of water-glycerol mixtures have been determined. The measured heats (Q) very closely approximate the relative partial molar enthalpy of water ($\bar{L}_1$). The results are given in Tables C-1 and C-2 (Appendix C).

In the following discussion, subscripts 1 and 2 refer to water and glycerol respectively. We have taken the pure liquids as reference states so that the differential heats are equal to the corresponding $\bar{L}$ quantities. By the method of least squares, $\bar{L}_1$ can be expressed as a polynomial in the mole fraction of glycerol, x_2:

$$\bar{L}_1 = -26503\, x_2^2 + 133630\, x_2^3 - 307900\, x_2^4 + 331990\, x_2^5 - 135550\, x_2^6 \qquad [6.2\text{-}1]$$

and

$$\frac{d\bar{L}_1}{dx_2} = -53006\, x_2 + 400890\, x_2^2 - 1231600\, x_2^3 + 1659900\, x_2^4 - 813300\, x_2^5 \qquad [6.2\text{-}2]$$

For a binary system at constant temperature and pressure,

$$x_1\, d\bar{L}_1 + x_2\, d\bar{L}_2 = 0 \qquad \text{(Gibbs-Duhem equation)}$$

or

$$x_1 \left(\frac{d\bar{L}_1}{dx_2} \right) + x_2 \left(\frac{d\bar{L}_2}{dx_2} \right) = 0 \qquad [6.2\text{-}3]$$

That is,

$$\frac{d\bar{L}_2}{dx_2} = -\frac{x_1}{x_2} \left(\frac{d\bar{L}_1}{dx_2} \right) \qquad [6.2\text{-}4]$$

Using equation [6.2-2],

$$\frac{d\bar{L}_2}{dx_2} = 53006 - 453900\, x_2 + 1632500\, x_2^2 - 2891500\, x_2^3 + 2473200\, x_2^4 - 813300\, x_2^5. \qquad [6.2\text{-}5]$$

$$\bar{L}_2 = \int \left(\frac{d\bar{L}_2}{dx_2} \right) dx_2 \qquad [6.2\text{-}6]$$

Thus,

$$\bar{L}_2 = 53006\, x_2 - 226950\, x_2^2 + 544170\, x_2^3 - 722870\, x_2^4 + 494640\, x_2^5 - 135550\, x_2^6 + I, \qquad [6.2\text{-}7]$$

where I is the integration constant.

When $x_2 = 1$, $\bar{L}_2 = 0$. (by definition)

Hence, $I = -6446$.

i.e.,

$$\bar{L}_2 = 53006\, x_2 - 226950\, x_2^2 + 544170\, x_2^3 - 722870\, x_2^4 + 494640\, x_2^5 - 135550\, x_2^6 - 6446. \qquad [6.2\text{-}8]$$

Since

$$\Delta H_{mix} = n_1 \bar{L}_1 + n_2 \bar{L}_2 \qquad [J] \qquad [6.2\text{-}9]$$

or

$$H^E = x_1 \bar{L}_1 + x_2 \bar{L}_2 \qquad [J/mol] \qquad [6.2\text{-}10]$$

we obtain

$$H^E = -6446\, x_2 + 26503\, x_2^2 - 66817\, x_2^3 + 102640\, x_2^4 - 82980\, x_2^5 + 27100\, x_2^6. \qquad [6.2\text{-}11]$$

The above H^E function is plotted in Fig. 6-1 and 6-2.

Because of the limitation of the apparatus, only $\bar{L}_1$ measurements were taken. Nevertheless, the correctness of the $\bar{L}_2$ expression derived from $\bar{L}_1$ by the Gibbs-Duhem equation is assured by checking the heat of solution of glycerol in water at infinite dilution ($x_2 = 0$) reported in the International Critical Tables (NRC, 1929). The reported value, $\bar{L}_2$ at $x_2 = 0$, is -6.3 kJ per mole solute (temperature not specified , believed to be about 20 °C), which is very close to the value calculated by the derived expression ($\bar{L}_2^{\infty}$, calc = -6.4 kJ.mol^{-1}, at 25 °C; agreed to within 2%). The heats of mixing in the water-glycerol system at temperature between 15 and 20 °C compiled in the International Critical Tables

(NRC, 1929) are also in good agreement with values calculated from the H^E expression derived from our data. This is illustrated in Table 6-1.

Table 6-1 Heats of mixing in the water-glycerol system

x_2	H^E (lit.)* /[J.mol^{-1}] (15 - 20°C)	H^E (calc) /[J. mol^{-1}] (25°C)
0.0077	-48	-48
0.0149	-88	-90
0.0208	-117	-123
0.0306	-166	-174
0.0600	-292	-304
0.0984	-430	-432
0.1370	-507	-525
0.2435	-649	-667
0.3588	-714	-722
0.5199	-678	-695

* Literature values adapted from the International Critical Tables (NRC,1929).

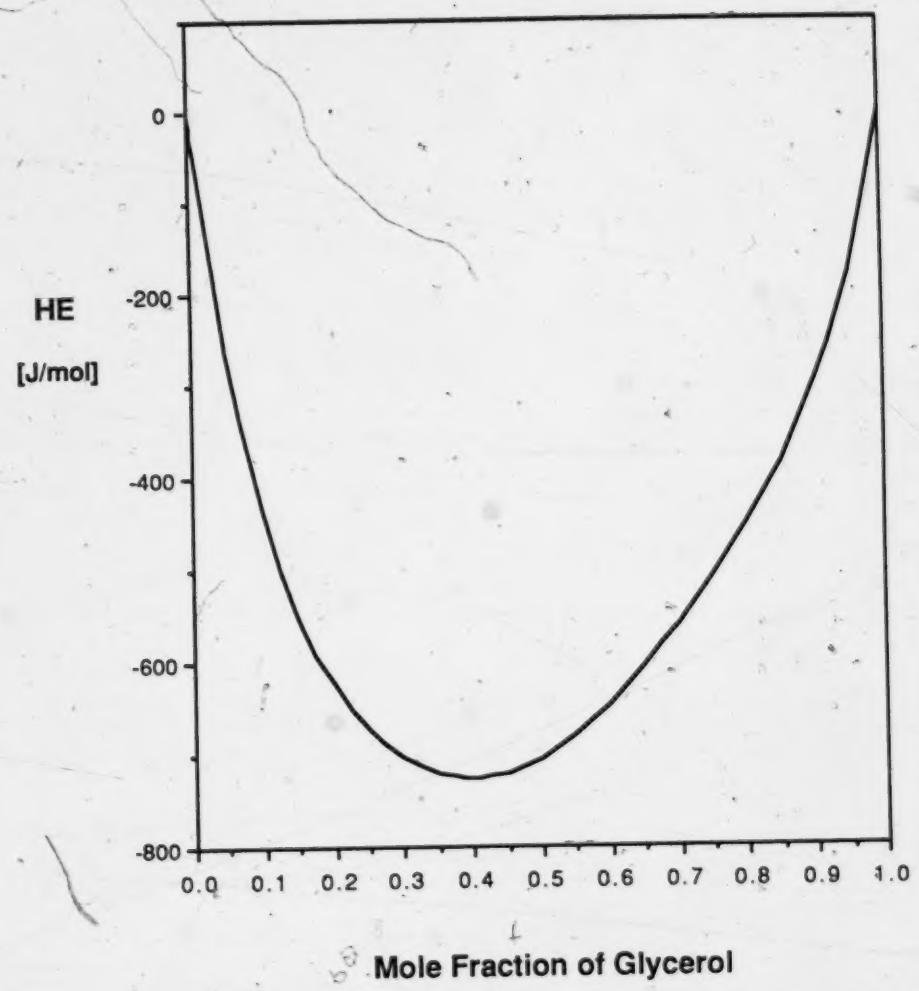

Fig.6-1 Excess enthalpy of water-glycerol system at 25 °C

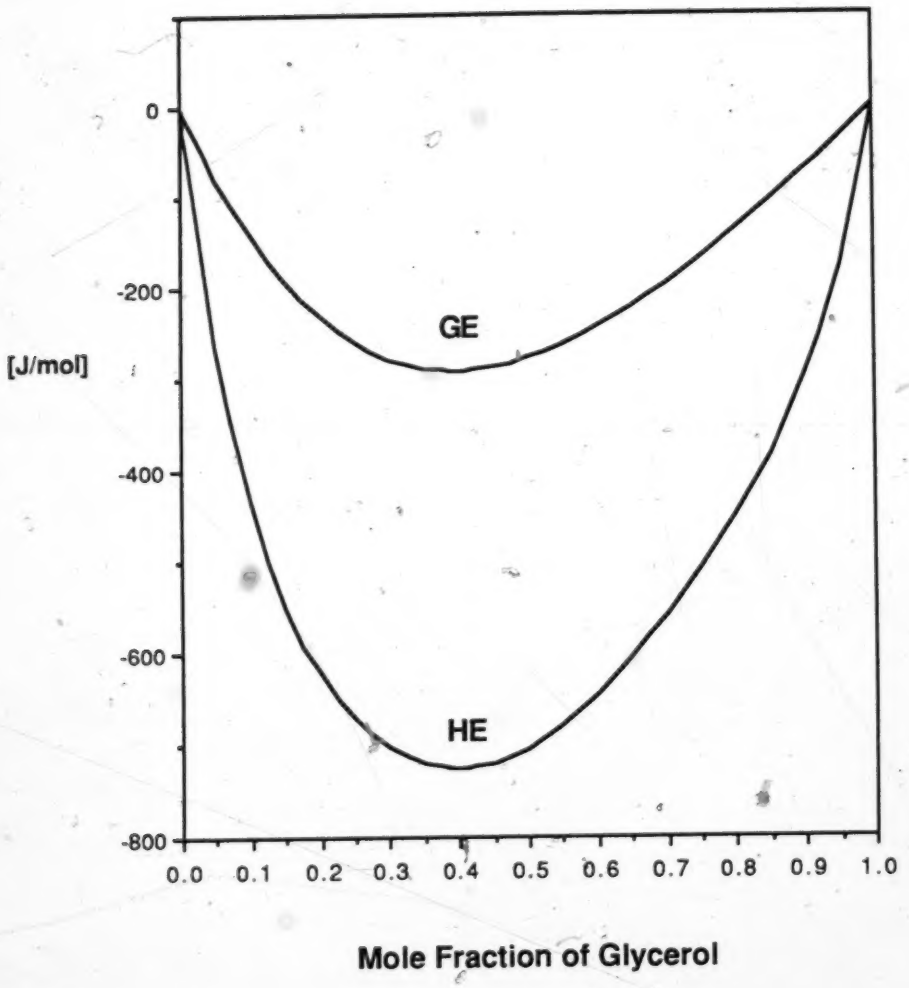

Fig 6-2 Excess Gibbs energy and excess ethalpy of water-glycerol system at 25 °C (G^E data adapted from Scatchard et al.,1938; and Kirgintsev and Luk'yanor,1982)

Chapter 7 Optimization of the UNIQUAC Parameters

Estimation of the parameters in mathematical models is often performed using a fairly simple empirical criterion. Alternatively, the parameter estimation may be performed using a more sophisticated criterion based on statistical considerations. This leads to the employment of optimization procedure.

The estimation operation is called optimal if the assignment of an estimate is in accordance with minimization of some criterion, or the objective function. Hence, an optimization procedure for parameter estimation generally involves the following two stages:

(1) Define an objective function which is a suitable measure of the departure of the data from the model, i.e., of the "lack of fit". For example, in the least squares method, the objective function is the sum of squares of residuals.

(2) Seek the optimal values of the parameters at which the objective function attains its minimum. The process of computing such optimum estimates is called optimization.

An optimization method which correctly treats the statistical behavior of the errors associated with all experimental observations always gives optimum estimates. However, this does not guarantee that the resulting estimates are the true values of the parameters. Therefore, in addition to the best estimates for the parameters, the optimization procedure should yield information useful in analysis of the "correctness" of the resulting estimates. Such consideration is incorporated in the optimization procedure developed for this study.

7.1 Optimization Method - Procedure and Methodology

According to the calculations performed in our group (Toupin, 1986; Choudhury, 1987; Lee,1987), simplex optimization has been shown to be a highly reliable and relatively efficient optimization procedure. This derivative-free, direct search method was originally devised by Spendley et al. (1962) and later developed by Nelder and Mead (1965a, b). The basic idea in the simplex method is to compare the values of the objective function at the n+1 vertices of a general simplex (formed by a set of n+1 points in n-dimensional space; n is the number of variables of a function) and move this simplex gradually towards the optimum point during the iterative process. The movement of the simplex is achieved by using three operations known as reflection, contraction and expansion (Nelder and Mead, 1965a, b). The simplex method of Nelder and Mead (1965a, b) is one of the most efficient pattern search methods currently available and has been found to work particularly well if the number of variables does not exceed five or six (Walsh, 1975; Shavers et al., 1979). As compared with other methods, it has turned out to be advantageous: it is not necessary to estimate first or higher order derivatives of the objective function; it is easy to follow the changes in the values of the objective function as the mininum is approached. In this study, the simplex procedure adapted by Toupin (1986) is used for the estimation of the UNIQUAC parameters. A detailed description of the simplex algorithm and accompanied computer program written in Fortran IV is provided by Toupin (1986).

A number of procedures have been proposed as criteria (or objective functions) for estimating parameters from multiresponse data. These have been summarized by Hunter (1967). In the present study two popular objective functions are evaluated and one of them is chosen for further optimization procedure.

The first objective function, proposed by Box and Draper (1965), is to minimize the determinant of the matrix of the sums of squares and cross products of the differences between the observed and predicted values of the responses. For example, using multiresponse data on G^E and H^E (2 response functions) to estimate the energy parameters, a_{12} and a_{21}, in the UNIQUAC equation, one would minimize the following 2x2 determinant with respect to a_{12} and a_{21}:

$$D = \begin{bmatrix} \sum_i (G_i^{expt} - G_i^{pred})^2 & \sum_i (G_i^{expt} - G_i^{pred})(H_i^{expt} - H_i^{pred}) \\ \sum_i (G_i^{expt} - G_i^{pred})(H_i^{expt} - H_i^{pred}) & \sum_i (H_i^{expt} - H_i^{pred})^2 \end{bmatrix} \qquad [7.1\text{-}1]$$

The second objective function is to minimize the sum of the weighted sums of squares of all the responses, the weighting factors, w_r, being the reciprocals of the variances.

$$S^2 = \sum_r w_r \sum_i (Y_{ri}^{expt} - Y_{ri}^{pred})^2, \qquad [7.1\text{-}2]$$

where r and i are the indices for responses and data points respectively.

By assuming that the percentage error is constant,

$$S^2 = \sum_r \sum_i \frac{1}{(Y_{ri}^{expt})^2} (Y_{ri}^{expt} - Y_{ri}^{pred})^2. \qquad [7.1\text{-}3]$$

The first objective function (D) is theoretically more versatile. It accounts for correlations between the responses, while the second one does not. Hence, lacking any special knowledge about a general multiresponse estimation problem, minimizing D is more appropriate.

In this study, however, it was found that the optimization method became less efficient and less reliable as D was applied to the adapted simplex optimization program (Toupin, 1986); convergence rate was low, more computer time was required and more faulty responses occurred. One possible reason is the convergence of |D| to a minimum is very sensitive to the starting values for the parameters (Ziegel and Gorman, 1980). (Preliminary parameter estimation thus seems to be necessary.) On the other hand, the second objective function (S^2) was found to give more reliable and rapid convergence. In terms of practical performance, the second objective function (S^2) is thus preferred.

Experimentally, the excess Gibbs energy and excess enthalpy are two independently determined quantities and they can be assumed to be two independent responses. Because of this, the use of the second objective function (S^2) in our optimization program is justified.

The optimization is carried out in two separate phases. The first phase is mainly devoted to the determination of the true q values of the six selected

compounds in order to evaluate the Q values of the building blocks. The second phase is simply the optimization of the two adjustable energy parameters for any aqueous carbohydrate system of interest.

Though only q_2 is the quantity desired in the first phase of optimization, three parameters (q_2, a_{12} and a_{21} for each binary system) are actually optimized. One major drawback of optimizing three parameters together is that the true value of q_2 is masked by the other two parameters.

As has been mentioned in section 4.1.1, $G^E_{(combinatorial)} \neq -TS^E$ but $G^E_{(combinatorial)} = -TS^E_{(athermal)}$. In other words, except if athermal entropic data are available (this would mean very high temperature entropic data of the mixture), q cannot be optimized separately using the entropic data alone without the inclusion of the two energy parameters in the optimization procedure. In order to screen out the interference effect from the energy parameters and to ensure the correctness of the q value obtained, a proper optimization scheme has to be developed.

One possible way is to use some subset of the data block to optimize only some of the parameters in the model while keeping other parameters constant. When good parameter estimates are available, all the data can then be used for estimating values for the parameters. Two observations (Appendix G) about the UNIQUAC equation may help to implement this idea:

(1) The H^E expression of UNIQUAC (equation [4.1-5]) is determined by q_i and the energy parameters, a_{ji}. The energy parameters are, indeed, the controlling parameters for the enthalpic contribution (Appendix G). Hence, a_{ji} can be optimized with q_i kept constant. If a good initial guess of q_i is supplied, good

estimates of a_{ji} will be obtained.

(2) Similarly, the TS^E expression (equation[4.1-7]) is largely determined by the structural parameters (Appendix G). If there is good estimation of a_{ji} from (1), a good estimate of q_i is highly possible.

Based on these two observations, the following optimization strategy is developed:

1. Optimize the energy parameters, a_{12} and a_{21}, using the H^E data alone; all other parameters are kept constant. The best initial guess of q_2 is given by Vera's method, and the subsequent values are obtained from step 2. The typical starting values for a_{12} and a_{21} would be (100., 100.), (-100, -100.) or (100., -100).
2. Set a_{12} and a_{21} to the optimized values obtained from step 1. and optimize q_2 using the TS^E data alone.
3. Repeat step 1. and 2. until the q_2, a_{12} and a_{21} values become stable.
4. Optimize q_2, a_{12} and a_{21} simultaneously using both the G^E and H^E data. The starting values for q_2, a_{12} and a_{21} are the final optimized values from step3.

This iterative process is found to be reliable and effective, as illustrated in Table 7-1 where the aqueous glucose solution is used as an example. From the good fitting of the excess functions and the small standard error of q_2, we may conclude that a good estimate of q_2 is obtained. This scheme is highly effective in determining the true value of q (but not the a_{ji}) because it reduces the interference effect from the energy parameters to a minimum. However, due to the high correlation existed between a_{12} and a_{21}, the standard errors for the energy parameters are relatively high, i.e., the estimates for a_{12} and a_{21} are not precise.

Table 7-1 Optimization of the q value of glucose using the iterative approach

System: H_2O (1) + Glucose (2) Temperature = 298.15K

Parameter values: $r_1 = 0.73$ * ; $r_2 = 4.998$ * ; $q_1 = 1.19$ * .

Response Functions	Optimized Parameters	q_2	a_{12}	a_{21}
H^E	a_{12}, a_{21}	3.998* (100.)	148.21	(-100.) -158.39
TS^E	q_2	(3.998) 5.333	148.21	-158.39
H^E	a_{12}, a_{21}	5.333	(148.21) 186.85	(-158.39) -160.27
TS^E	q_2	(5.333) 5.179	186.85	-160.27
H^E	a_{12}, a_{21}	5.179	(186.85) 186.72	(-160.27) -161.42
TS^E	q_2	(5.179) 5.201	186.72	-161.42
H^E	a_{12}, a_{21}	5.201	(186.72) 186.76	(-161.42) -161.26
#G^E,H^E	q_2,a_{12},a_{21}	(5.201) 5.293	(186.76) 218.12	(-161.26) -174.95

Note:Values in parentheses ( ) are the starting values for optimization; subscripts 1,2 indicate water and glucose molecules respectively; * values calculated from Vera's method. For r_2 and q_2, Vw(OH) = 8.04 cm^3/mol (Bondi's value) is used instead of the value 4.59 cm^3/mol proposed by Abusleme and Vera, 1985;

%RMSD of G^E = 2.59%; %RMSD of H^E = 2.32%;

Standard error: $\sigma(q_2) = 0.027$; $\sigma(a_{12}) = 7.06$; $\sigma(a_{21}) = 3.01$.

A general problem encountered with all optimization methods is a false convergence at a point other than the minimum. This difficulty has been found in using the simplex method (Nelder and Mead, 1965). Another difficulty is to assess the correctness of the parameters obtained. Merely refining the convergerce criterion would often involve needless evaluations, and in some cases could still be ineffective. Hence, measures of reliability for the calculated results have been incorporated in Toupin's simplex program. These measures aim at assessing 1). a real optimum and 2). parameter significance, uniqueness and error.

A real optimum can be indicated by a) a comparison between the actual S^2 value and the calculated S^2 value, b) goodness of fit, and c) the standard error of the parameters. When the region of the optimum has been reached, the modified simplex program by Toupin (1986) fits a quadratic approximation to the response to enable the optimum to be located more precisely. A S^2 value (the calculated S^2 value) can be calculated from this quadratic fitting. At the same time, another S^2 value (the actual S^2 value) which is calculated directly from the predicted and experimental values of the excess functions can be obtained. If these two S^2 values are identical, an optimum is found. It is also helpful to note the goodness of fit either by graphical method (plotting and examining residues) or by comparing the predicted values with the experimental values through some statistics such as RMSD or %RMSD. Usually, the standard errors of the parameters indicate how well the parameter value is located.

The correctness of the q parameter obtained from the optimization program is assessed by a) the variance-covariance matrix, b) the correlation matrix, and c) the linear relation between r and q in a family of compounds. The diagonal elements of the variance-covariance matrix approximate the variances of the corresponding parameters, while the off-diagonal elements of the matrix represent the covariances between different parameters. The square roots of these variances are estimates of the standard errors in the parameters and, in effect, are a measure of their uncertainties. The correlation coefficients between parameters can be calculated from the variances and covariances. It is known that the energy parameters, a_{12} and a_{21}, are highly correlated, but they should not be highly correlated with q. Hence, in the optimization of q_2, a_{12} and a_{21}, it is expected that the correlation coefficients between a_{12} and a_{21} should be above 0.98 and the correlation coefficients between q_2 and a_{12} or a_{21} should be much less than 0.9. Any other combinations of correlation coefficients may only indicate false convergences. Based on molecular considerations, Vera et al. (1977) have already demonstrated the linear relation between van der Waals volumes and surfaces in a family of compounds. Since r is directly related to the van der Waals volume and q to the van der Waals surface, this linearity may directly imply a linear correlation between r and q. In other words, the validity of the optimized q values of a family of compounds (except isomers) can be assessed by the existence of the linear relation between r and q. This will be shown in section 7.2.

7.2 Optimization Results and Evaluation of the New Structural Parameter Values

The evaluation of the Q values of the building blocks requires the q values of ethylene glycol, glycerol, mannitol, xylose, glucose and fructose (see section 5.2.3). The q_2 and the corresponding energy parameters were optimized with the modified simplex procedure (section 7.1) using experimental data on the excess Gibbs energy, excess enthalpy and excess entropy of aqueous solutions of the six selected compounds at 25°C. The optimized q_2, a_{12} and a_{21} values are given in Table 7-2.

Table 7-2 The optimized q_2, a_{12} and a_{21} values

System *	q_2	a_{12}	a_{21}
H_2O (1) + EG (2)	2.095	338.74	-268.52
H_2O (1) + GLY(2)	2.914	354.87	-263.80
H_2O (1) + MAN(2)	5.612	184.82	-140.74
H_2O(1) + XYL(2)	4.618	222.49	-179.10
H_2O(1) + GLU(2)	5.293	218.12	-174.95
H_2O(1) + FRU(2)	5.413	182.96	-150.87

* EG = Ethylene Glycol ; GLY = Glycerol; MAN = Mannitol; XYL = xylose;

GLU = Glucose; FRU = Fructose.

subscript : 1 = H_2O (solvent); 2 = solute.

As mentioned in section 7.1, the validity of the optimized q values can be assessed by the existence of the linear relation between r and q in a family of compound. Fig. 7-1 shows the plotting of the r and q values of the polyols. The linearity clearly indicates the correctness of the optimized q values.

Recall

$$\begin{bmatrix} 2 & 0 & 0 & 0 \\ 2 & 1 & 0 & 0 \\ 2 & 4 & 0 & 0 \\ 0 & 4 & 0 & 1 \\ 1 & 4 & 0 & 1 \\ 1.25 & 2.75 & 1 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6 \end{bmatrix} \qquad [5.2\text{-}12]$$

b_1 = q (ethylene glycol) = 2.095

b_2 = q (glycerol) = 2.914

b_3 = q (mannitol) = 5.612

b_4 = [q (xylose) - Q (CH_2)] = (4.618 - 0.431) = 4.187

b_5 = [q (glucose) - Q (CH)] = (5.293 - 0.182) = 5.111

b_6 = [q (fructose) - Q (CH_2) - Q (CH)] = 5.044

The modified Gram-Schmidt (MGS) method is used to solve this overdetermined system. The method computes the least-squares solution of the system and consists of reducing the normal equations to a simpler form. The computer subroutine is available from TEAPACK (Johnston, 1982) as well as IMSL (1980) library.

The solution was found to be:

$x_1 = 1.025 = Q(CH_2OH)$

$x_2 = 0.889 = Q(CHOH)$

$x_3 = 0.737 = Q(COH)$

$x_4 = 0.581 = Q(\text{-}O\text{-})$

As a result, the values of the structural parameters of all the building blocks are found and they are summarized in Table 7-3.

Table 7-3 The R and Q values of the building blocks

Type	Structural Unit	R	Q
linkage	-O-	0.541	0.581
hydroxyl	CH_2OH	0.966	1.025
	CHOH	0.783	0.889
	COH	0.601	0.737
Alkyl *	CH_2	0.541	0.431
	CH	0.358	0.182
	C	0.176	0.0

* The R and Q values of the alkyl groups are calculated as described in section 5.2.3.

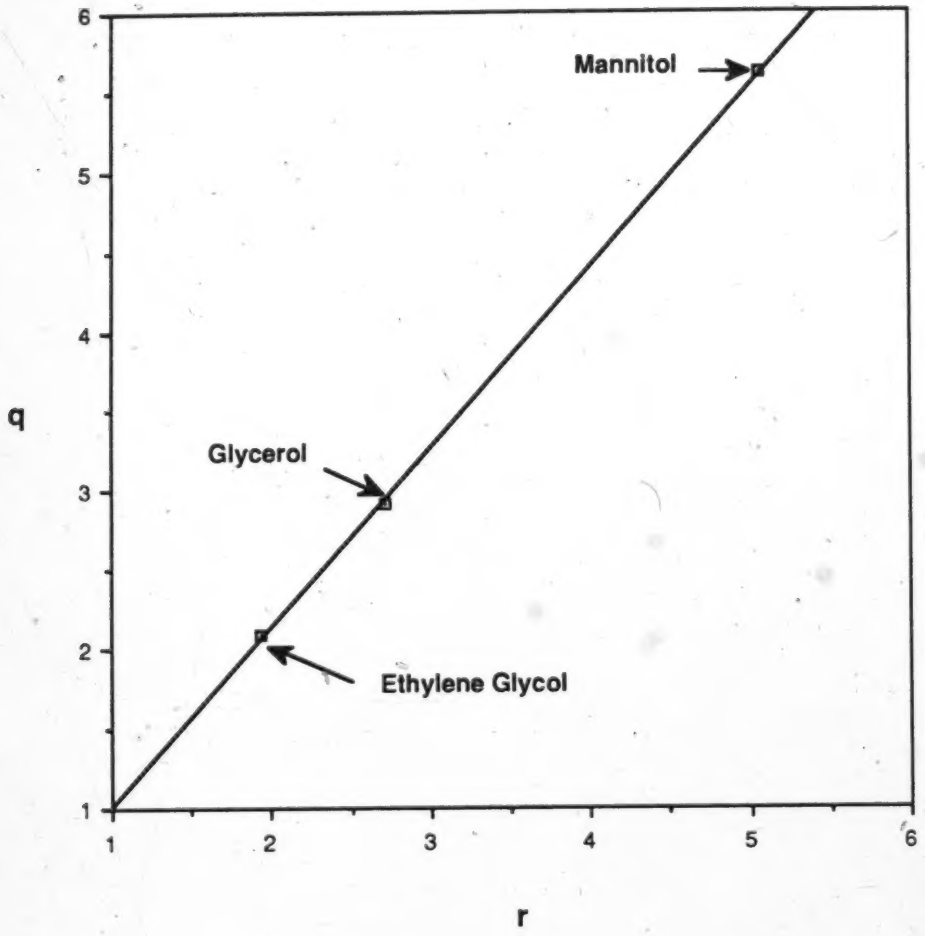

Fig.7-1 Correlation between r and q for polyols

Chapter 8 Representation and Prediction of the Thermodynamic Properties of Aqueous Carbohydrate Solutions using the New Parameters

The correctness of the optimized parameters has been checked by the optimization procedure described in chapter 7. Nevertheless, the correctness of the new parameters of other carbohydrate molecules calculated from the building block values is not assured. Hence, the validity of these new calculated parameters has to be tested. This can be done by considering 1) the theoretical validity of the parameters and 2) the performance of the UNIQUAC equation using the new set of parameters. The theoretical validity of the structural parameters may be indicated by the linear relation existed between r and q values of non-isomers in a family as mentioned by Vera et al. (1977). Similarly, the correlation of the energy (or interaction) parameters proposed by Luecke (1983) and confirmed by Millan et al. (1987) would be a good indicator for testing the validity of the energy parameters. The performance of the model can be evaluated in the following two aspects:

a) the simultaneous representation of the G^E and H^E functions, and
b) the prediction of other physical properties, such as freezing point depression, solubility, etc.

The five aqueous carbohydrate systems selected for this validation process are the aqueous solutions of:

1) xylose (monosaccharide; pentose),
2) glucose (monosaccharide; hexose; structural isomer of fructose),

3) fructose (monosaccharide; hexose; structural isomer of glucose),

4) sucrose (disaccharide),

5) raffinose (oligosaccharide).

The r_2 and q_2 values of these carbohydrate molecules are calculated using the R and Q values given in Table 7-3; the r_1 and q_1 values of water molecule is set to be 0.73 and 1.19 (Vera et al., 1977) respectively. The new structural parameters of the selected carbohydrate molecules are presented in Table 8-1. The two adjustable energy parameters (a_{12} and a_{21}) are simply determined by optimization using both the G^E and H^E data. The result is summarized in Table 8-1.

Table 8-1 Parameters of five simple carbohydrates by building block method

Compound	r_2	q_2	a_{12}	a_{21}
Xylose	4.214	4.568	206.86	-172.19
Glucose	4.998	5.344	231.29	-180.51
Fructose	4.998	5.413	182.96	-150.87
Sucrose	9.686	9.809	121.52	-111.68
Raffinose	14.374	14.433	122.88	-106.68

Note: subscripts 1 and 2 refer to water and the carbohydrate molecule concerned.

As shown in Fig. 8-0, the carbohydrate compounds lie perfectly on the same straight line with only a slight discrepancy found between the two isomers, glucose and fructose. This clearly indicates that the building block method does give theoretically consistent values.

By studying the (A_{12}, A_{21}) values published in the DECHEMA Data Series (Gmehling and Onken, 1977), Luecke (1983) confirmed that there is a high degree of correlation between interaction (or energy) parameters in the UNIQUAC equation, and he proposed the following equation:

$$(A_{12} + c)\,(A_{21} + c) = 2 \times 10^6, \qquad [8.0\text{-}1]$$

where c is a constant, and $A_{ji} = (u_{ji} - u_{ii}) = R\,a_{ji}$. For example, in water-ethanol system, c is found to be 1290 when A_{12} and A_{21} are given in cal mol^{-1}.

In our case, both a_{12} and a_{21} are known, hence, c can be solved for each aqueous carbohydrate system. The c values of the five aqueous carbohydrate systems are given in Table 8-2.

A t-test is performed to test the difference between the c values and their mean value. The computed t values of the two extreme c values, 1429.0 and 1416.4, are 1.483 and -1.273 respectively. For 95 percent confidence interval, the critical t-value with 4 degree of freedom is 2.776. Since the absolute values of our computed t's are less than the critical t-value, we may conclude that all the five c values are not significant different from the mean c value.

Another t-test is performed to test the difference between the highest c value and the lowest c value. The computed t is 2.756, while the critical t-value

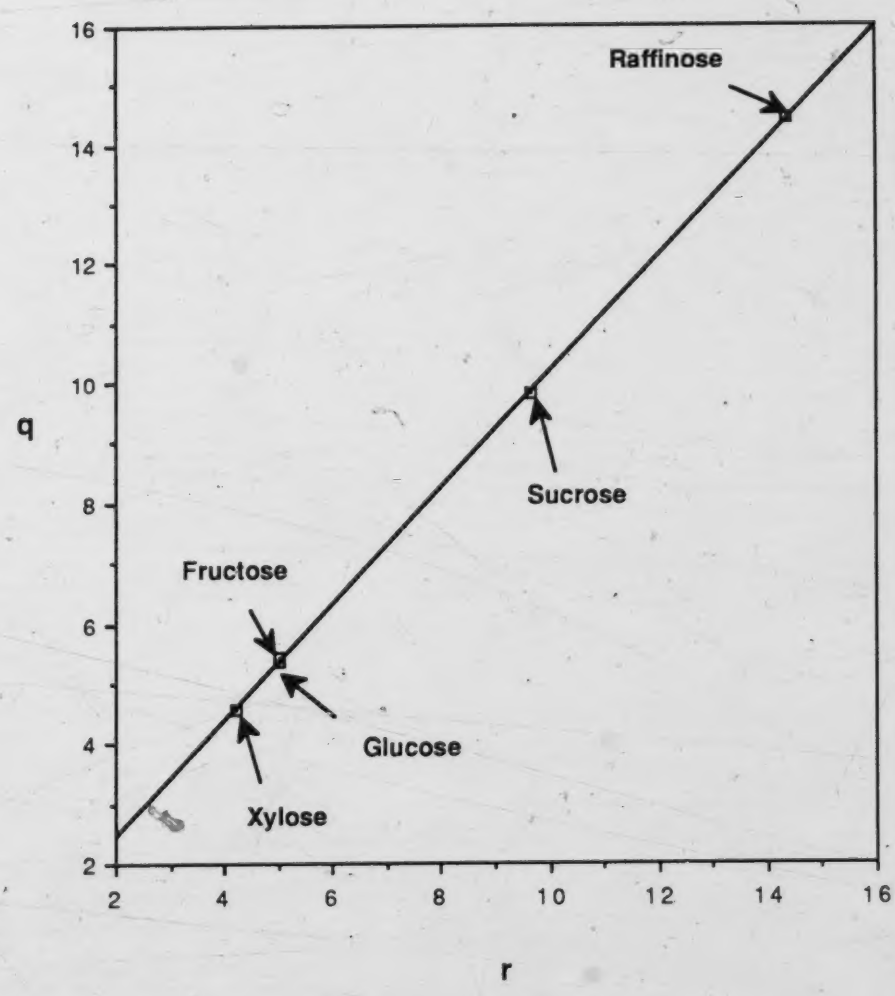

Fig. 8-0 Correlation between r and q for carbohydrates

Table 8-2 A_{12}, A_{21} and c values of aqueous carbohydrate systems

System	a_{12} [K]	a_{21} [K]	A_{12} [cal/mol]	A_{21} [cal/mol]	c [cal/mol]
Xylose	206.86	-172.19	411.07	-342.18	1429.0
Glucose	231.29	-180.51	459.62	-358.71	1421.7
Fructose	182.96	-150.87	363.58	-299.81	1420.7
Sucrose	121.52	-111.68	241.49	-221.93	1423.3
Raffinose	122.88	-106.68	244.19	-212.00	1416.4

mean c = 1422.22

(α = 0.05 and d.f. = 4) is 2.776 (>2.756). Hence, it may be concluded that all the five c values are not significantly different. If c is not a variable, the relation between A_{12} and A_{21} (equation [8.0-1]) would be the same for all five systems studied. The fact that the energy parameters are consistently correlated, as proposed by Luecke (1983), demonstrates the validity of the energy parameters determined in this study.

8.1 Representation of the Excess Properties

It is well known that the original UNIQUAC equation is unable to represent the excess Gibbs energy and excess enthalpy simultaneously with satisfactory results (Renon, 1985; Skjold-Jorgensen et al., 1980), and it generally fails to give an accurate representation of the thermodynamic properties of highly nonideal system (Zou and Prausnitz, 1987; Brandani and Evangelista, 1984; Nath and Bender, 1981; Anderson and Prausnitz, 1978). It is thus critical to test the performance of the equation using the new sets of parameters evaluated by the building block method. The simultaneous representations of the excess Gibbs energy and excess enthalpy for the five aqueous carbohydrate solutions (water-xylose, water-glucose, water-fructose, water-sucrose, and water-raffinose systems) at 25 °C are shown in Fig. 8-1 to 8-5b. The resulting simultaneous representation is remarkedly successful (%RMSD is well within 4%, see Table 8-4).

Since Vera's evaluation method has already been demonstrated to be an improved method over the original one (section 5.1), calculations have been made using this method. The UNIQUAC parameters evaluated by Vera's method for the five aqueous carbohydrate solutions are presented in Table 8-3.

As illustrated in Fig. 8-6 to 8-10b, Vera's approach is still unable to represent the excess properties of aqueous solutions of carbohydrates simultaneously with reasonable results. Fig. 8-6 to 8-10b and Table 8-4 show that the building block method has an absolute superiority over Vera's method.

It has been mentioned that Vera's method is not suitable for complex molecules. This limitation is clearly indicated in Table 8-4 where the fitting by Vera's method becomes worse as the molecule becomes more complicated. This limitation is not found in the building block method; the mean deviations for the five carbohydrate systems have been consistently maintained to a relatively low level, even for more complicated structures such as raffinose.

Table 8-3 Parameters of five simple carbohydrates by Vera's method

Compound	r_2	q_2	a_{12}	a_{21}
Xylose	3.49	2.79	-5065.1	-143.1
Glucose	4.09	3.27	-919.6	-114.7
Fructose	4.09	3.27	-5063.1	-120.4
Sucrose	8.23	6.38	-5103.7	-96.5
Raffinose	12.37	9.49	-4945.5	-94.3

Note: subscripts 1 and 2 refer to water and the carbohydrate molecule concerned.

Table 8-4 Mean deviations (%RMSD) of simultaneous representation of G^E and H^E data

	%RMSD			
	Building Block Method		Vera's Method	
System	G^E	H^E	G^E	H^E
Xylose	2.13	0.94	10.03	7.41
Glucose	3.00	3.55	21.44	4.89
Fructose	2.95	3.06	25.02	28.10
Sucrose	1.12	3.93	47.81	53.39
Raffinose	3.50	3.66	76.75	134.55

Note:

$$\%\text{RMSD} = \sqrt{\frac{\sum_{i=1}^{n} \left(1 - \frac{Y_i^{calc}}{Y_i^{expt}}\right)^2}{n}} \times 100 ,$$

where Y_i = G^E or H^E data,

n = number of data points.

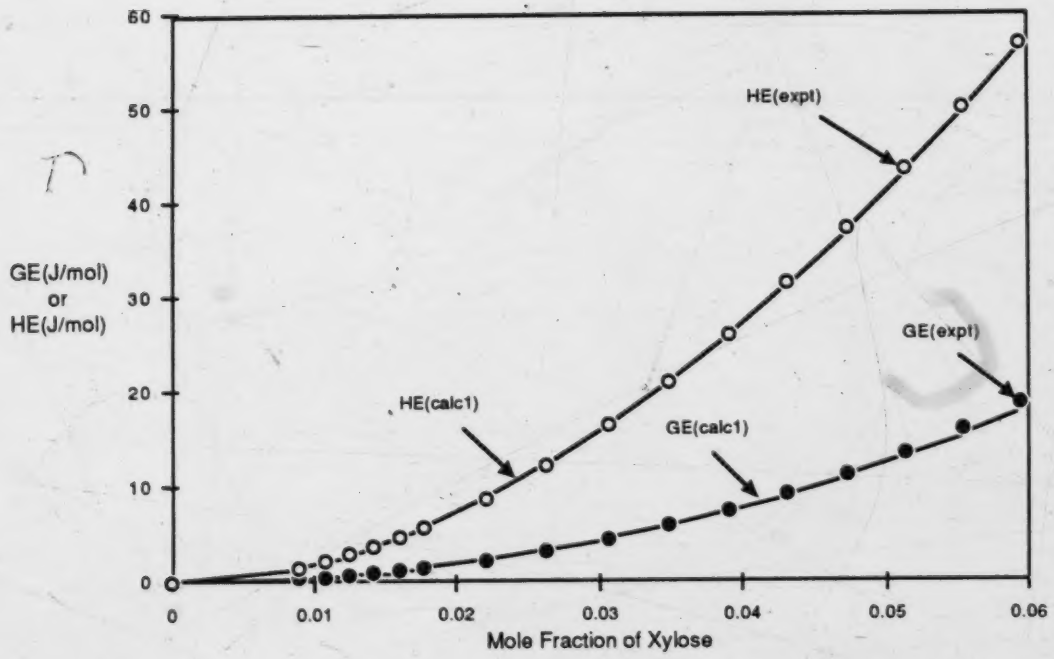

Fig. 8-1 Simultaneous representation of the excess Gibbs energy, GE, and excess enthalpy, HE, for the system water-xylose at 25^{0}C. Predicted values calculated from the UNIQUAC equation with revised parameters by the building block method; experimental data adapted from Barone et al., 1981; Uedaira and Uedaira, 1970 and 1969; Barone et al., 1982.

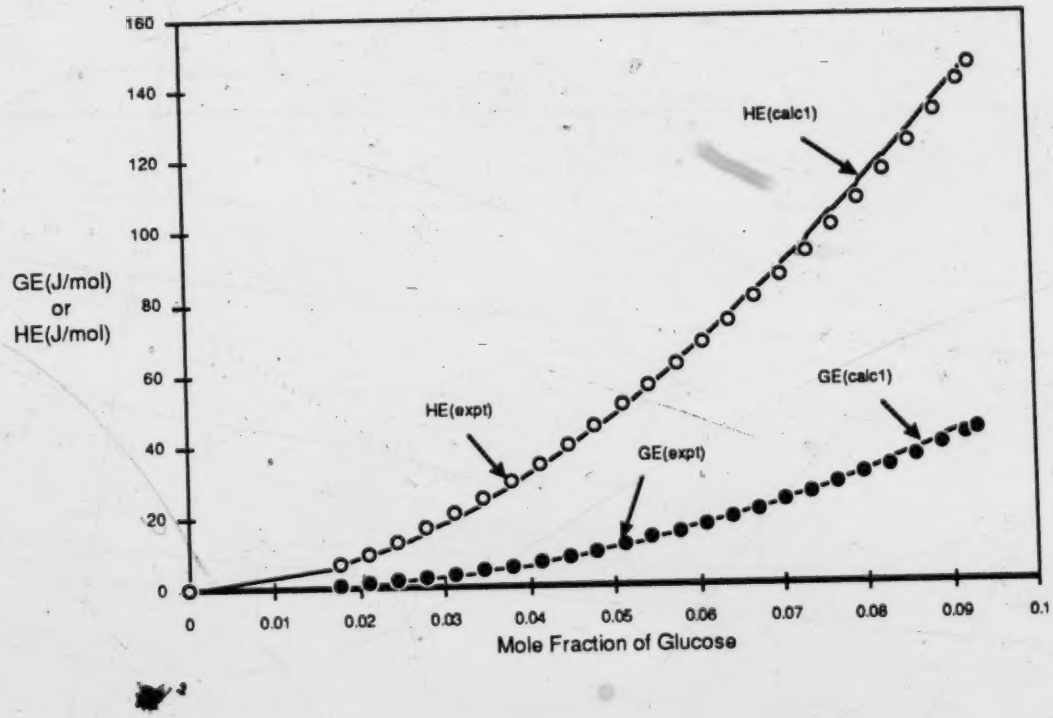

Fig. 8-2 Simultaneous representation of the excess Gibbs energy, GE, and excess enthalpy, HE, for the system water-glucose at 25^{0}C. Predicted values calculated from the UNIQUAC equation with revised parameters by the building block method; experimental data adapted from Taylor and Rowlinson, 1955; Stokes and Robinson, 1966.

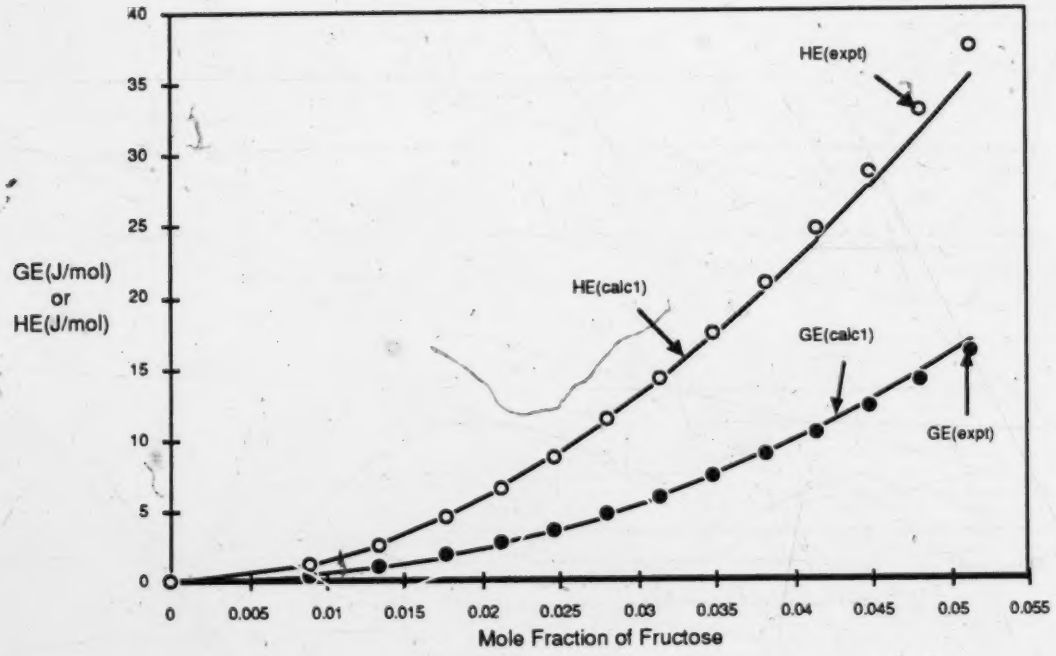

Fig. 8-3 Simultaneous representation of the excess Gibbs energy, GE, and excess enthalpy, HE, for the system water-fructose at 25^{0}C. Predicted values calculated from the UNIQUAC equation with revised parameters by the building block method; experimental data adapted from Barone et al., 1981; Barone et al., 1986.

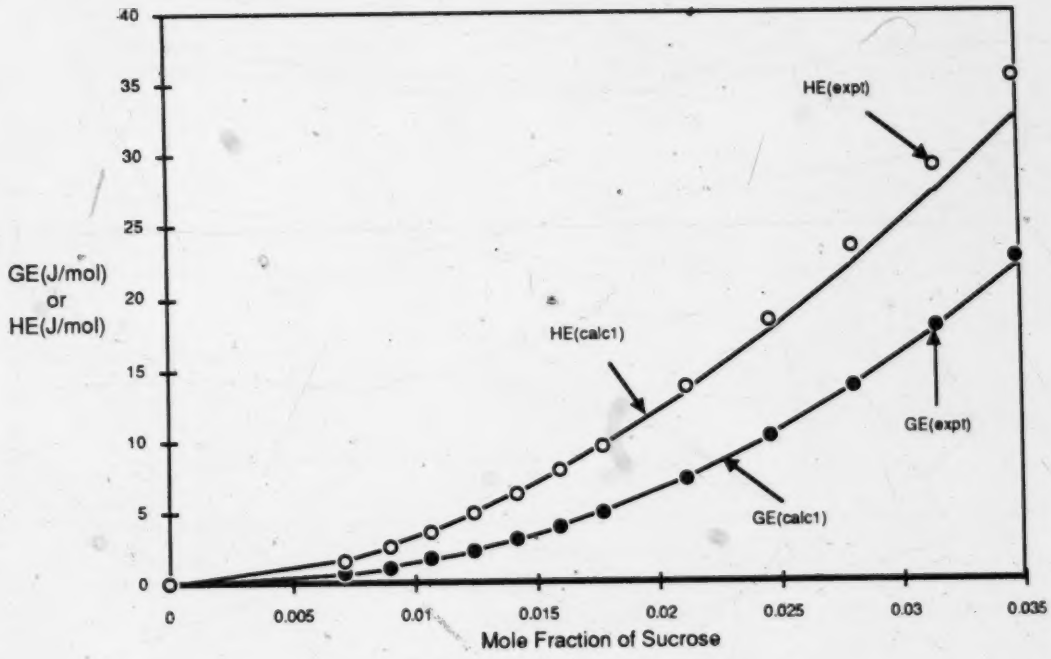

Fig. 8-4 Simultaneous representation of the excess Gibbs energy, GE, and excess enthalpy, HE, for the system water-sucrose at 25^{0}C. Predicted values calculated from the UNIQUAC equation with revised parameters by the building block method; experimental data adapted from Barone et al., 1981; Savage and Wood, 1976; Robinson and Stokes, 1961.

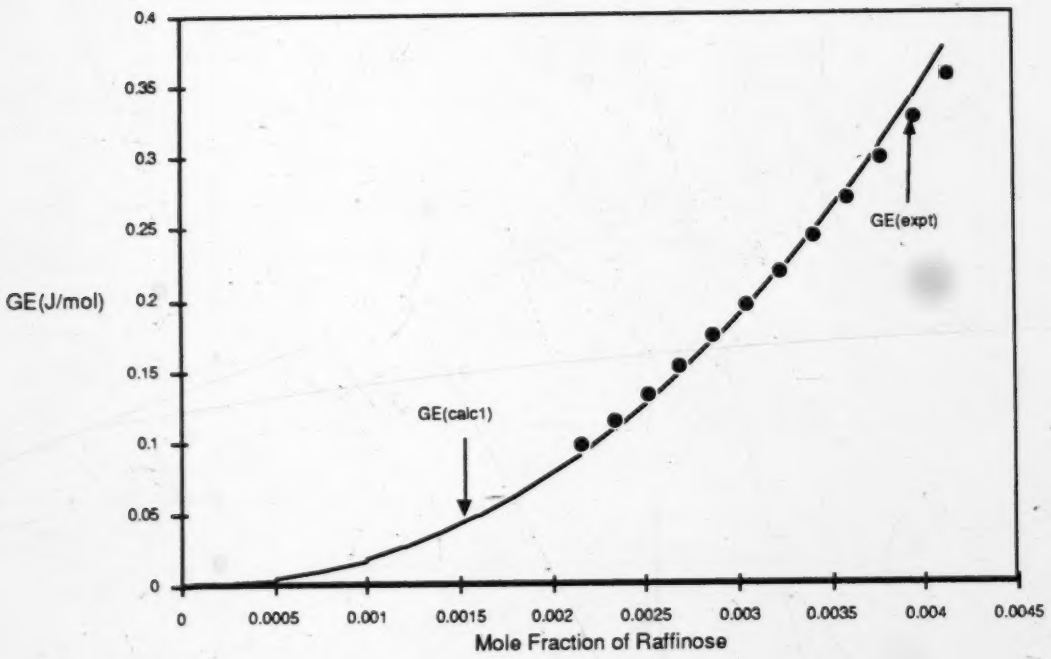

Fig. 8-5a Representation of the excess Gibbs energy, GE, for the system water-raffinose at 25^{0}C. Predicted values calculated from the UNIQUAC equation with revised parameters by the building block method; experimental data adapted from Ellerton et al., 1964.

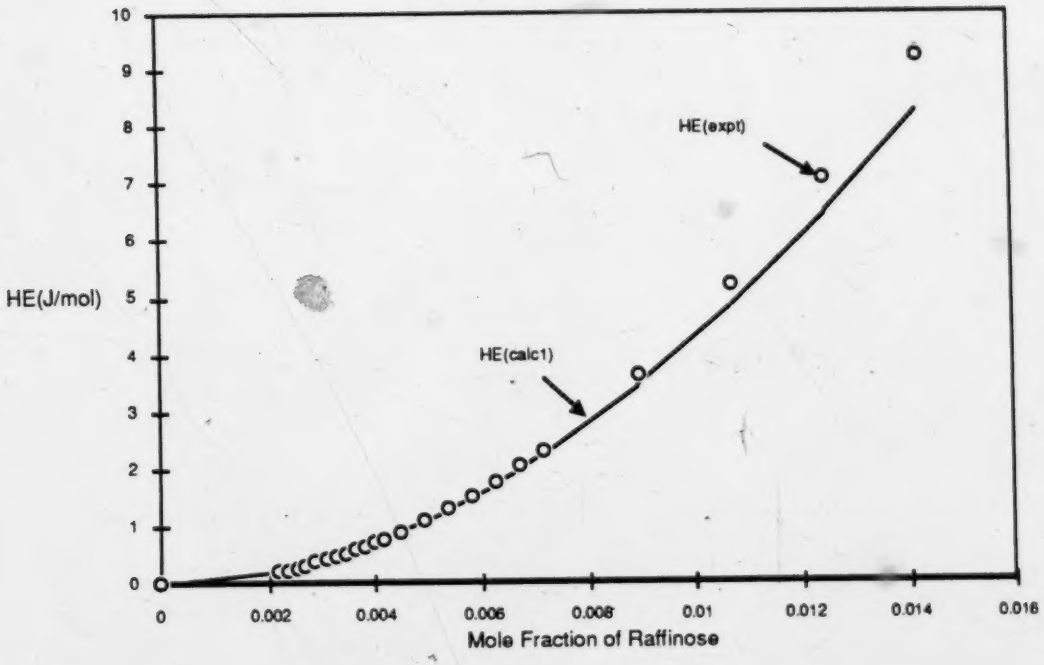

Fig. 8-5b Representation of the excess enthalpy, HE, for the system water-raffinose at 25^{0}C. Predicted values calculated from the UNIQUAC equation with revised parameters by the building block method; experimental data adapted from Barone et al., 1981.

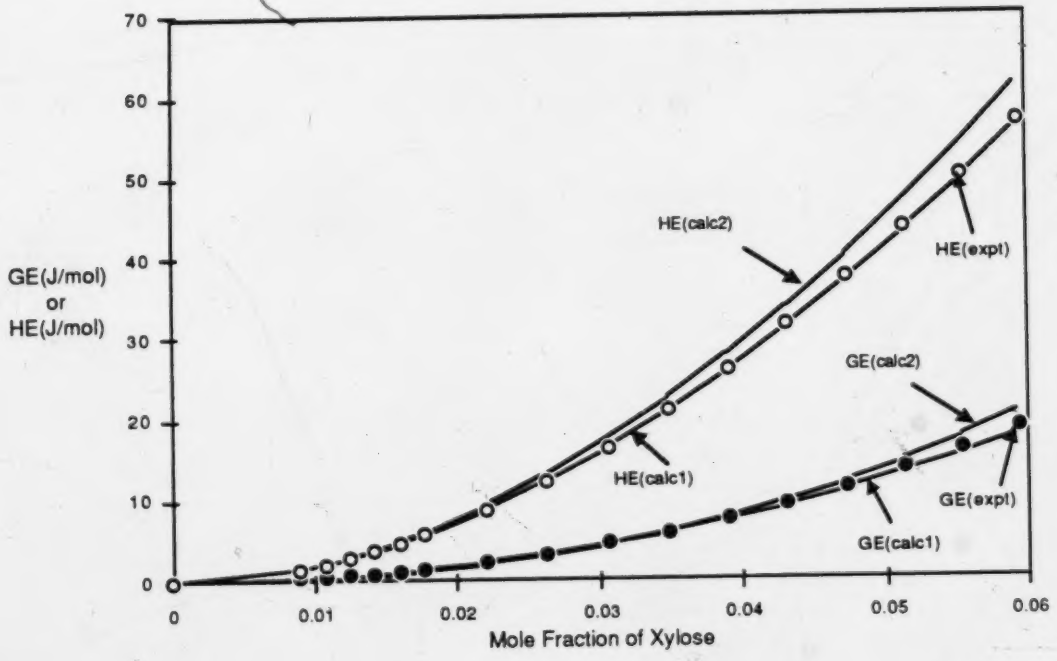

Fig. 8-6 Experimental and calculated GE and HE data for the system water-xylose at 25^{0}C. G(calc1) and H(calc1) calculated from UNIQUAC using the building block approach; G(calc2) and H(calc2) calculated from UNIQUAC using Vera's approach. Experimental data adapted from Barone et al., 1981; Uedaira and Uedaira, 1970 and 1969; Barone et al., 1982.

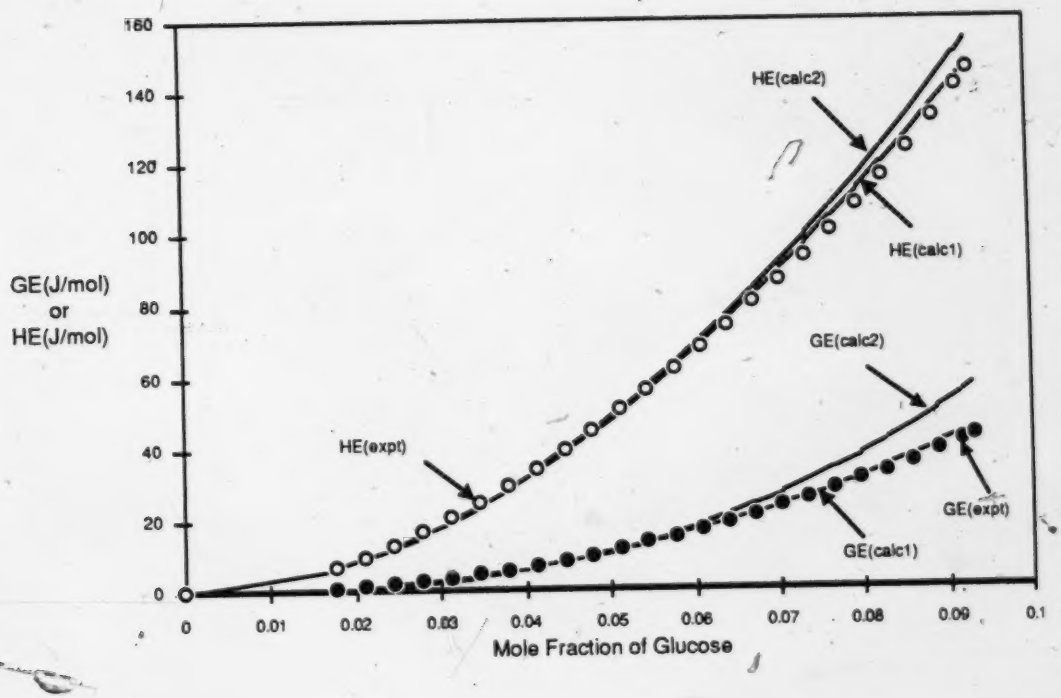

Fig. 8-7 Experimental and calculated GE and HE data for the system water-glucose at 25^{0}C. G(calc1) and H(calc1) calculated from UNIQUAC using the building block approach; G(calc2) and H(calc2) calculated from UNIQUAC using Vera's approach. Experimental data adapted from Taylor and Rowlinson, 1955; Stokes and Robinson, 1966.

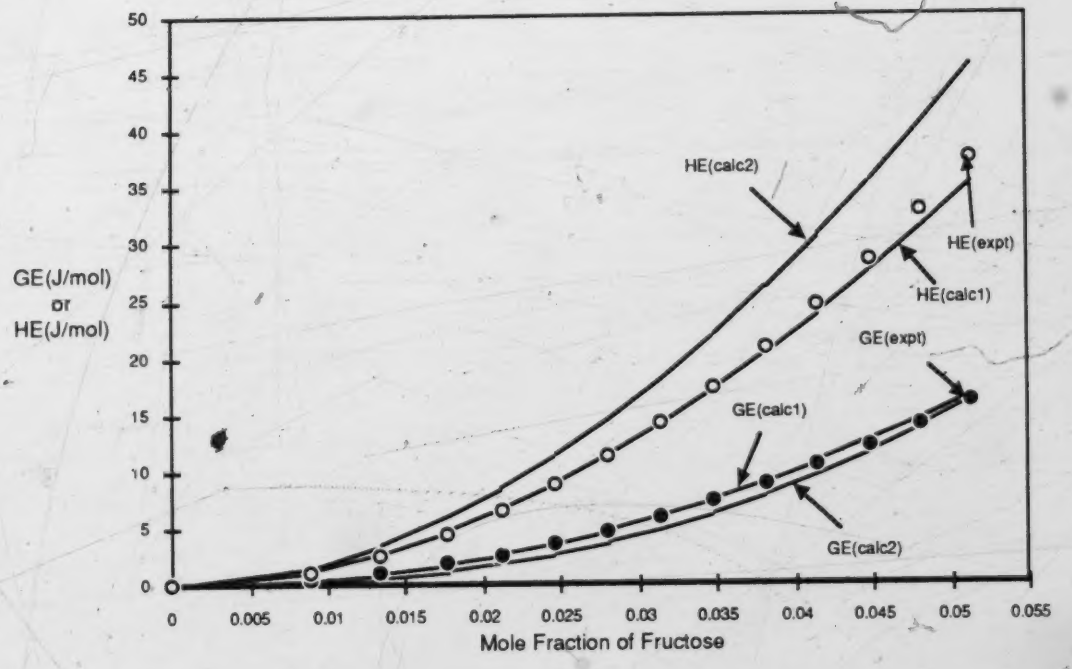

Fig. 8-8 Experimental and calculated GE and HE data for the system water-fructose at 25°C. G(caic1) and H(calc1) calculated from UNIQUAC using the building block approach; G(calc2) and H(calc2) calculated from UNIQUAC using Vera's approach. Experimental data adapted from Barone et al., 1981; Barone et al., 1986.

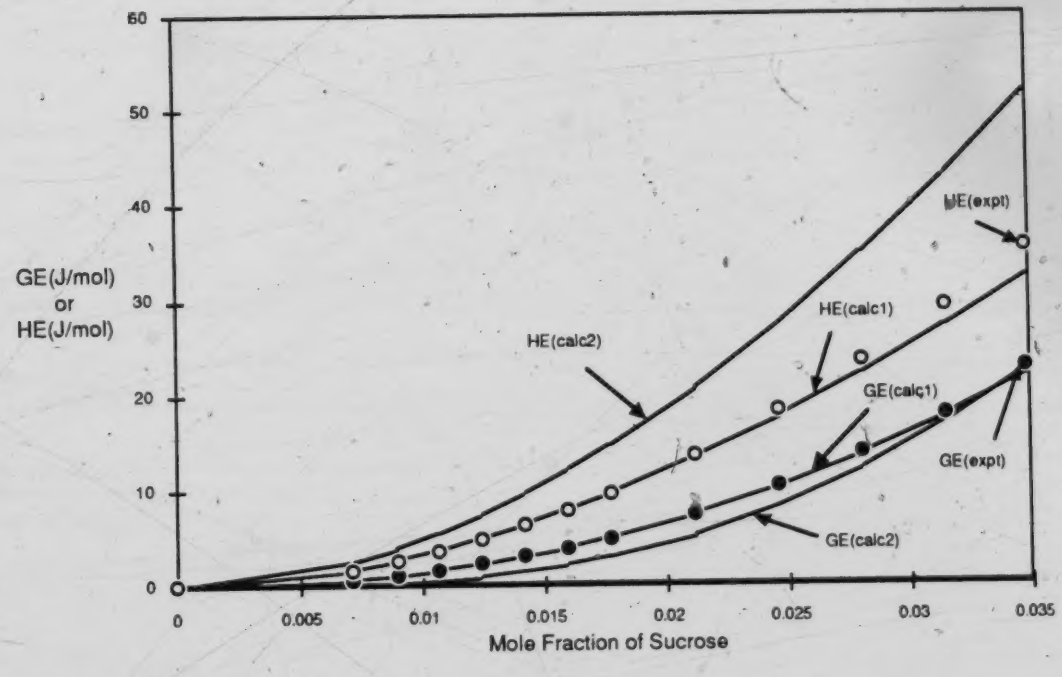

Fig. 8-9 Experimental and calculated GE and HE data for the system water-sucrose at 25^{0}C. G(calc1) and H(calc1) calculated from UNIQUAC using the building block approach; G(calc2) and H(calc2) calculated from UNIQUAC using Vera's approach. Experimental data adapted from Barone et al., 1981; Savage and Wood, 1976; Robinson and Stokes, 1961.

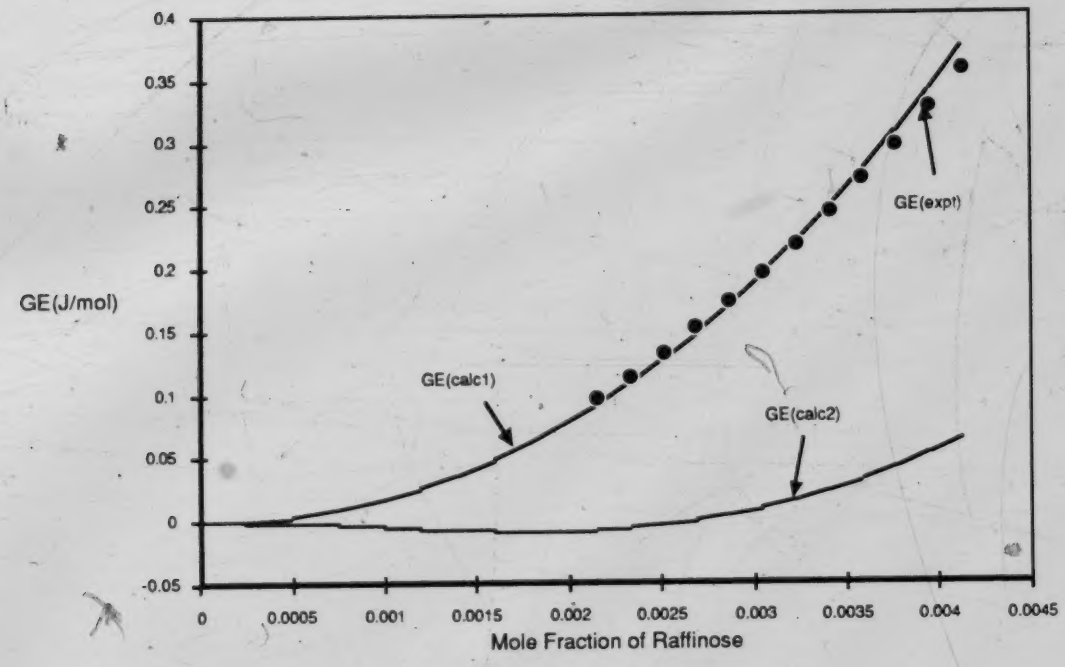

Fig. 8-10a Experimental and calculated GE data for the system water-raffinose at 25^{0}C. G(calc1) calculated from UNIQUAC using the building block approach; G(calc2) calculated from UNIQUAC using Vera's approach. Experimental data adapted from Ellerton et al., 1964.

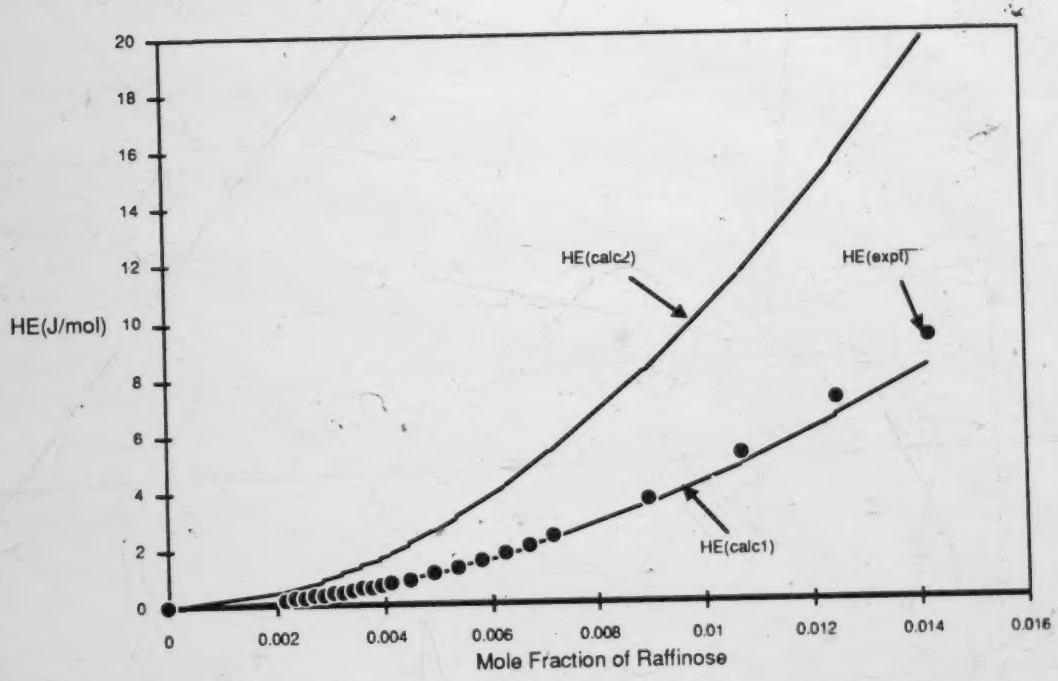

Fig. 8-10b Experimental and calculated HE data for the system water-raffinose at 25^{0}C. H(calc1) calculated from UNIQUAC using the building block approach; H(calc2) calculated from UNIQUAC using Vera's approach. Experimental data adapted from Barone et al., 1981.

8.2 Prediction of Freezing Point Depression

The validity of the new parameters evaluated by the building block method is further tested by their ability to predict some physical properties such as freezing point depression and solubility.

The temperature at which crystals of pure solvent are in equilibrium with a solution depends on the activity of the solvent in the solution (Klotz and Rosenberg, 1974). Therefore, the freezing point depression due to the addition of solute can be estimated by the knowledge of changes in activity of the solvent. The variation of the solid activity (a_s) with temperature at constant pressure is given by the relation:

$$\left(\frac{\partial \ln a_s}{\partial T} \right)_P = \frac{\Delta H_f}{RT^2}, \qquad \text{(Wall, 1974)} \qquad [8.2\text{-}1]$$

where ΔH_f is the enthalpy of fusion.

If the solvent is water, the water activity (a_w) is related to the freezing point depression (δ) by the following expression:

$$-\ln a_w = 9.6916 \times 10^{-3}\ \delta + 4.95 \times 10^{-6}\ \delta^2 + \ldots \qquad [8.2\text{-}2]$$

(Klotz and Rosenberg, 1974)

Detailed discussion of the derivation of the above relations is given by Klotz and Rosenberg (1974).

The expression [8.2-2] has been used to calculate the freezing point depressions of the aqueous solutions of glucose, fructose and sucrose. The predicted and experimental values for these three systems are plotted in Fig. 8-11 to 8-13. The predictions for the aqueous solutions of glucose and fructose are found to be excellent with %RMSD of less than 1%. The prediction for aqueous sucrose solution is also good with %RMSD = 4.2%.

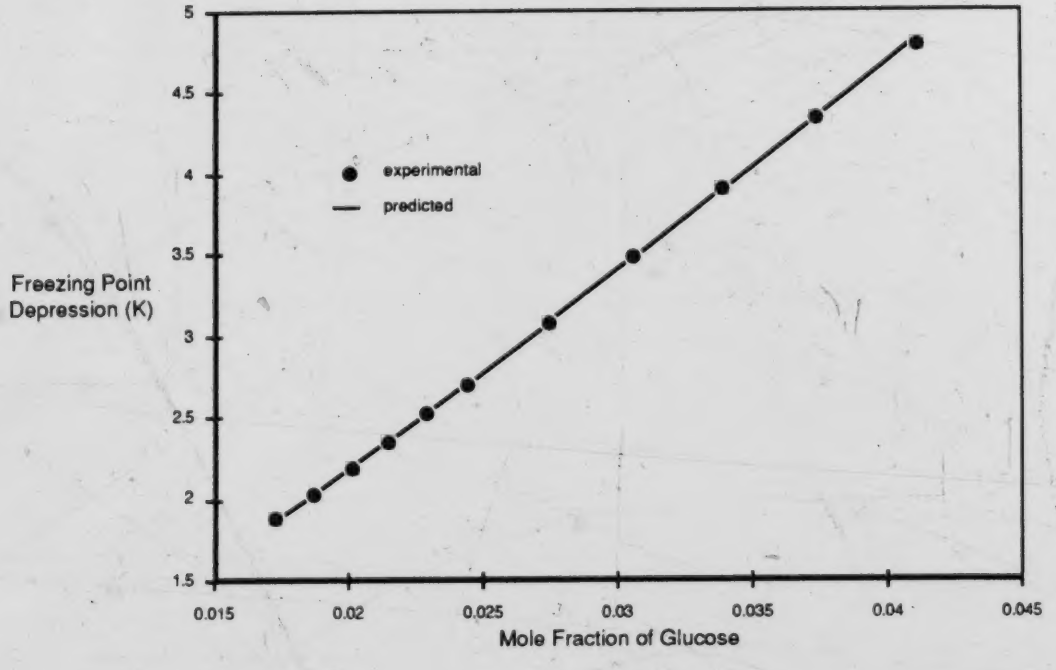

Fig. 8-11 Predicted and experimental freezing point depression of aqueous glucose solutions. Experimental data adapted from CRC (1983-1984) tables on freezing point depression.

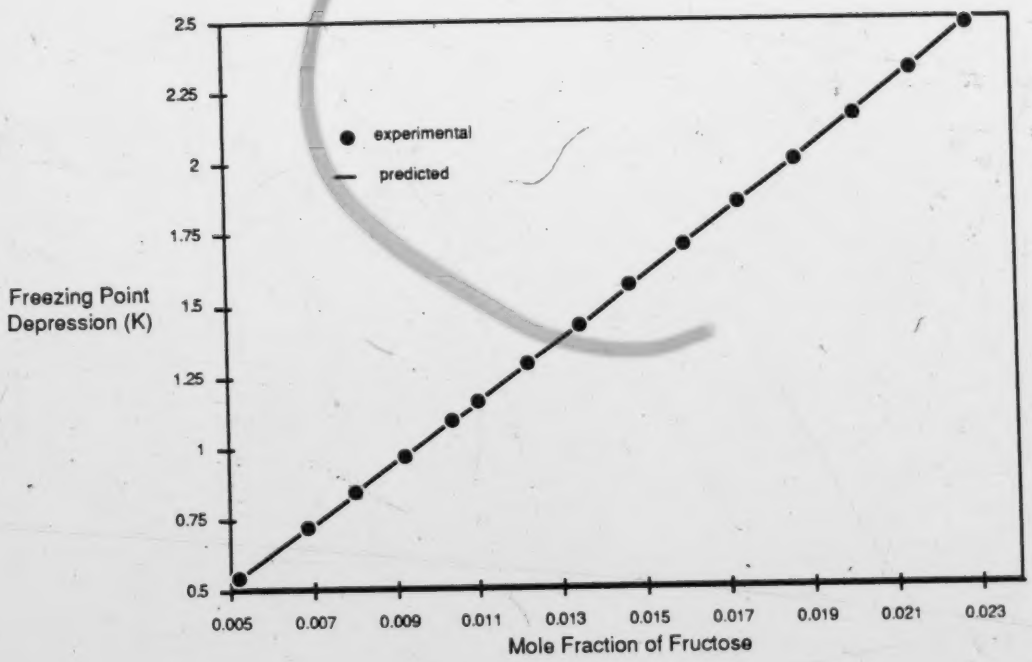

Fig. 8-12 Predicted and experimental freezing point depression of aqueous fructose solutions. Experimental data adapted from CRC (1983-1984) tables on freezing point depression.

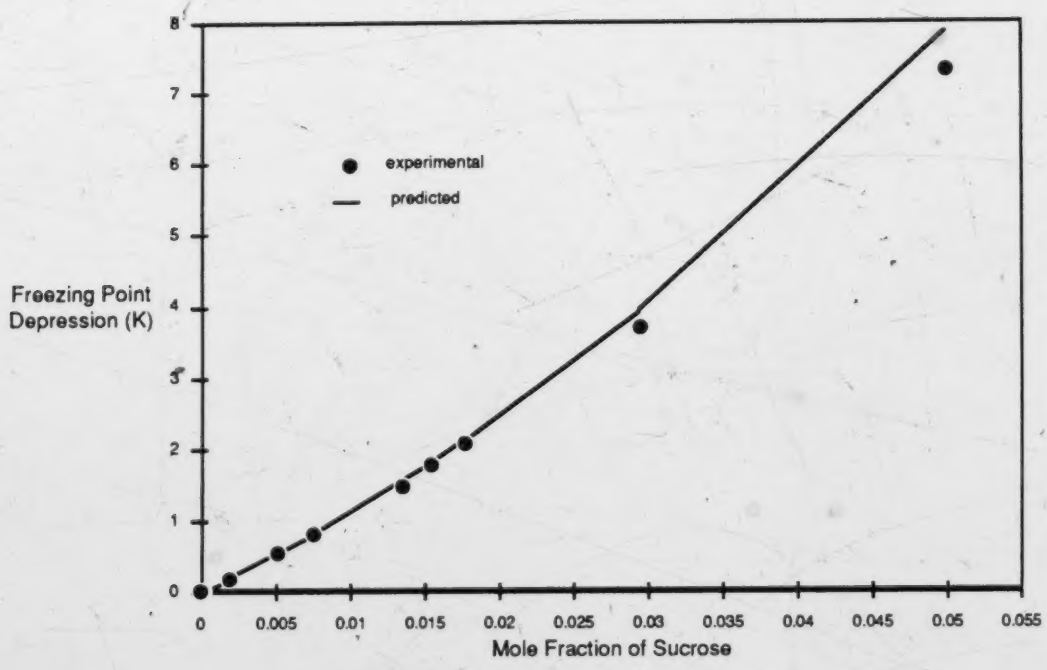

Fig. 8-13 Predicted and experimental freezing point depression of aqueous sucrose solutions. Experimental data from Honig (1953)

8.3 Prediction of Solubility

One basic method to estimate the solubility of a solid solute in a liquid solvent at any temperature was proposed by Reid et al. (1977). Assume that the solid phase is pure. At temperature T, the solubility (mole fraction) x_2 can be estimated by

$$\ln \gamma_2 x_2 = \frac{-\Delta H_f}{RT}\left(1 - \frac{T}{T_m}\right), \qquad \text{(Reid et al.,1977)} \qquad [8.3\text{-}1]$$

where ΔH_f is the enthalpy of fusion of the solute; T_m is the normal melting temperature. The standard state for activity coefficient of the solute, γ_2, is pure (subcooled) liquid 2 at system temperature T.

Substituting $\Delta S_f = (\Delta H_f / T_m)$, we obtain

$$\ln \gamma_2 x_2 = \frac{-\Delta S_f}{R}\left(\frac{T_m}{T} - 1\right), \qquad [8.3\text{-}2]$$

where ΔS_f is the entropy of fusion.

Generally, the enthalpies of fusion of most carbohydrates are not available in the literature, thus the advantage of equation [8.3-2] over [8.3-1], in addition to its greater simplicity, is that ΔS_f is more predictable than ΔH_f. The entropies of fusion of glucose and fructose are estimated by equation [8.3-2] using one single solubility data. The ΔS_f of glucose has been estimated to be 67.4 J mol^{-1} K^{-1}, and the ΔS_f of fructose is 55.3 J mol^{-1} K^{-1}.

For molecules having n > 5 nonhydrogen atoms, Yalkowsky and Valvani (1980) proposed the following relation to estimate entropy of fusion based on a geometric interpretation of the melting process:

$$\Delta S_f = 13.5 + 2.5\,(n - 5)\ \text{eu.} \qquad [8.3\text{-}3]$$

From the above relation, the entropy of fusion of glucose and fructose would be 16 eu. or 66.9 J mol^{-1} K^{-1} (since n=6 for both compounds). This computed ΔS_f value is very close to the two estimated ΔS_f values, thus insures the estimation made for glucose and fructose.

Knowing the ΔS_f values, the solubility can be calculated from equation [8.3-2]. The predicted and experimental glucose and fructose solubilities are shown in Fig. 8-14 and 8-15 respectively. Good prediction is obtained with %RMSD for glucose and fructose = 3.5% and 4.3% respectively.

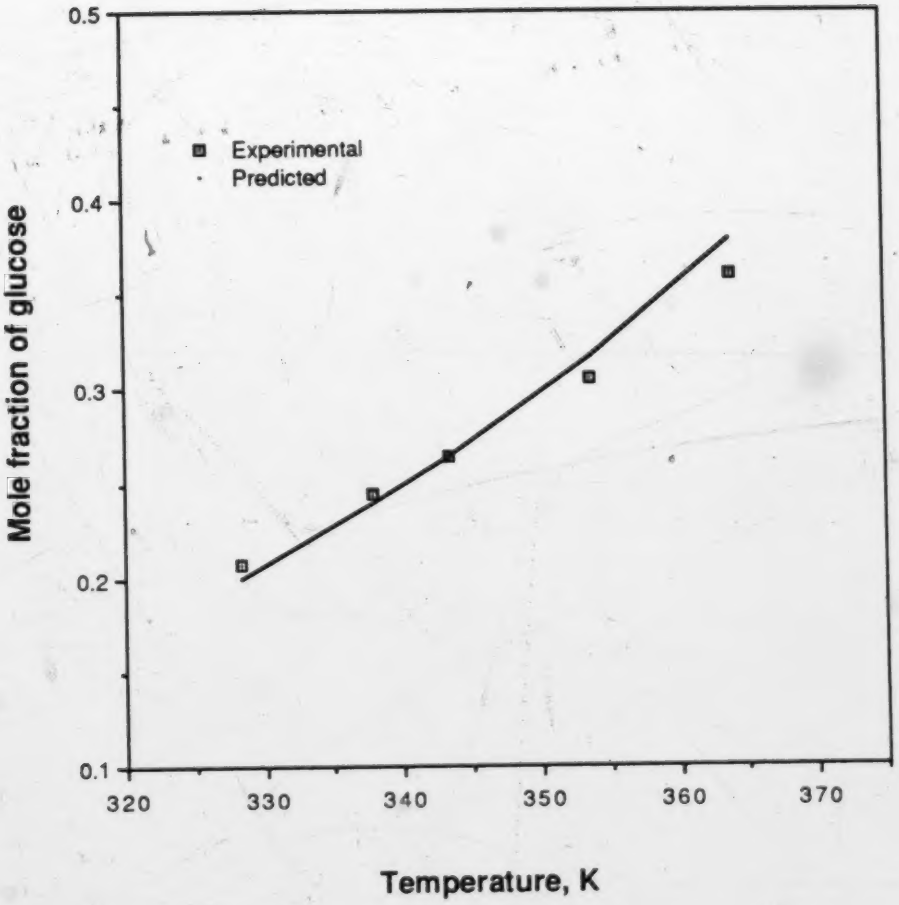

Fig. 8-14 Predicted and experimental solubility of glucose in water. Experimental data adapted from Honig (1953).

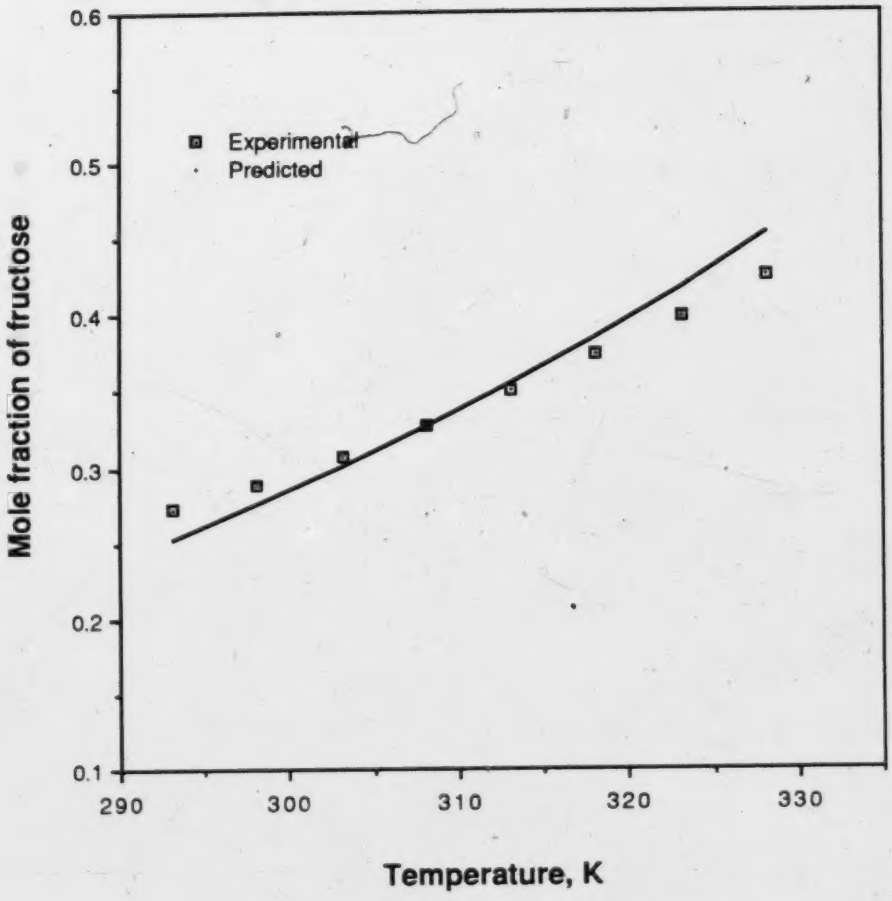

Fig. 8-15 Predicted and experimental solubility of fructose in water. Experimental data adapted from Honig (1953).

Chapter 9 Conclusion and Recommendations

There is a need for an accurate thermodynamic representation of aqueous food solution in food engineering. Through a survey of current available models for the excess Gibbs energy, the UNIQUAC model is shown to be the most reliable and versatile thermodynamic model. However, according to our analysis, the applicability of the model to aqueous carbohydrate solutions is severely limited by the improper estimation of the structural parameters. In order to rectify the deficiencies of the original evaluation method, a new evaluation method called the building block method is developed and new parameters for water and carbohydrate molecules are determined. The new parameters have been shown to be theoretically consistent and valid. Another estimation method proposed by Vera et al. (1977) is also evaluated. The method is demonstrated to be an improved version over the original method. However, it is not applicable to complex molecules such as carbohydrates. Practically, the building block method has an absolute superiority over Vera's method regarding aqueous carbohydrate solutions.

The capability of the UNIQUAC model to describe the highly nonideal behavior of aqueous carbohydrate solutions has been successfully extended by the use of the building block method developed in this study. This is shown by the significant improvement on simultaneous representation of the excess Gibbs energy and excess enthalpy of aqueous carbohydrate solutions, and on prediction of other physical properties such as freezing point depression and solubility.

The present successful result on binary water-carbohydrate systems may encourage us to attempt more complex systems such as ternary or higher order systems. However, this may require a much broader data base including ternary or high order experimental data to evaluate the two adjustable binary energy parameter, a_{ij}, for each binary. Unfortunately, experimental data on aqueous carbohydrate solutions are quite limited, except some common sugars, and data on ternary or higher order systems are even scarce. Hence, much more efforts are needed in obtaining reliable experimental data on these systems.

This, indeed, leads us to recognize one major weakness of the UNIQUAC equation: experimental data are required to evaluate the energy parameters. There are two possible solutions. The first is to look for some simple direct physical measurements that can give reliable measure of the energy parameters, as well as make use of the correlation between the energy parameters to reduce evaluation efforts. This requires a thorough investigation on the physical and theoretical significance of the energy parameters in the UNIQUAC model. The second, perhaps the ultimate solution, is a UNIFAC-like approach, i.e., not only values for the structural parameters are determined for the building blocks, but also values for the energy parameters.

Carbohydrate is only one major constituent in food solutions; there are other important constituents like protein, amino acids, fatty acids, minerals, etc. It is our dream that the same concept can be applied to all the other significant compounds important to food solutions. If that is the case, future calculations will be simplified to just the manipulation of a limited number of building blocks.

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APPENDICES

APPENDIX A: Summary of experimental correlations for excess functions

Correlations obtained by fitting empirically the experimental data as polynomial expressions greatly facilitate the use of numerical techniques for the optimization of the model parameters. The following summarizes the experimental correlations for the excess functions of various aqueous systems studied:

A.1 WATER/ETHYLENE GLYCOL SYSTEM (adapted from Villamanan et al., 1984)

Correlation of all data is through the four-parameter Margules equation,

$$H^E / (x_1 x_2 R T) = A'_{21} x_1 + A'_{12} x_2 - (C'_{21} x_1 + C'_{12} x_2) x_1 x_2 \quad [A.1\text{-}1]$$

$$G^E / (x_1 x_2 R T) = A_{21} x_1 + A_{12} x_2 - (C_{21} x_1 + C_{12} x_2) x_1 x_2 \quad [A.1\text{-}2]$$

$$S^E / (x_1 x_2 R) = (A'_{21} - A_{21}) x_1 + (A'_{12} - A_{12}) x_2 - [(C'_{21} - C_{21}) x_1 + (C'_{12} - C_{12}) x_2] x_1 x_2 \quad [A.1\text{-}3]$$

where x_1 and x_2 are the mole fractions of water and ethylene glycol respectively. The parameters (A_{ij} and C_{ij}) in the above equations are calculated by the following relations:

$$M_{ij} = M_{ij0} / T + M_{ij1} - M_{ij2} \ln T \qquad [A.1\text{-}4]$$

$$M'_{ij} = M_{ij0} / T + M_{ij2} , \qquad [A.1\text{-}5]$$

where M represents either A or C.

The constants in equations [A.1-4] and [A.1-5] are listed in Table A-1.

Table A-1 Constants in equations [A.1-4] and [A.1-5] for calculation of correlating parameters for water/ethylene glycol (adapted from Villamanan et al., 1984)

M_{ij0}	M_{ij1}	M_{ij2}
A_{210} = -2059.209	A_{211} = 31.24356	A_{212} = 4.33806
A_{120} = 258.827	A_{121} = -9.50026	A_{122} = -1.47594
C_{210} = -4535.562	C_{211} = 82.06843	C_{212} = 11.80013
C_{120} = -1994.695	C_{121} = 36.25889	C_{122} = 5.23041

A.2 WATER/GLYCEROL SYSTEM (at 25 °C)

By the method of least-squares, the experiment data of Scatchard et al. (1938), and Kirgintsev and Luk'yanov (1962) can be fitted as

$$\ln \gamma_1 = -1.284\, x_2^2 + 1.569\, x_2^3 - 0.585\, x_2^4, \qquad [A.2\text{-}1]$$

by use of the Gibbs-Duhem equation, we obtain

$$\ln \gamma_2 = -0.1005\, x_1^2 - 0.009\, x_1^3 - 0.585\, x_1^4 . \qquad [A.2\text{-}2]$$

As a result, G^E can be calculated by

$$G^E = R\,T\,(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \qquad [A.2\text{-}3]$$

From the isoperibolic calorimetric measurements,

$$H^E = -6446\, x_2 + 26503\, x_2^2 - 66817\, x_2^3 + 102640\, x_2^4 - 82980\, x_2^5 + 27100\, x_2^6 \qquad [A.2\text{-}4]$$

A.3 WATER/MANNITOL SYSTEM (at 25 °C)

$$H^{E(m)} = 69.9\, m^2 + 19.6\, m^3 \quad [J/kg] \quad \text{(Tasker and Wood, 1982)} \qquad [A.3\text{-}1]$$

$$G^{E(m)} = 8.428\, m^2 + 5.206\, m^3 \quad [J/kg] \quad \text{(Robinson and Stokes, 1961)} \qquad [A.3\text{-}2]$$

A.4 WATER/XYLOSE SYSTEM (at 25 °C)

$$H^{E(m)} = 339\ m^2 - 19\ m^3 \quad [J/kg] \quad \text{(Barone et al.,1981a)} \quad [A.4\text{-}1]$$

$$G^{E(m)} = 34\ m^2 + 2.8\ m^3 + 0.2\ m^4 \quad [J/kg] \quad \text{(Uedaira and Uedaira, 1969)} \quad [A.4\text{-}2]$$

A.5 WATER/GLUCOSE SYSTEM (at 25 °C)

$$H^{E(m)} = 343.2\ m^2 - 12.8\ m^3 \quad [J/kg] \quad \text{(Savage and Wood, 1976; Barone et al., 1981a)} \quad [A.5\text{-}1]$$

$$G^{E(m)} = 70\ m^2 - 0.8\ m^3 \quad [J/kg] \quad \text{(Stokes and Robinson, 1966; Barone et al., 1981a)} \quad [A.5\text{-}2]$$

A.6 WATER/FRUCTOSE SYSTEM (at 25 °C)

$$H^{E(m)} = 264\ m^2 - 7\ m^3 \quad [J/kg] \quad \text{(Barone et al., 1981a)} \quad [A.6\text{-}1]$$

$$G^{E(m)} = 61\ m^2 \quad [J/kg] \quad \text{(Barone et al.,1986)} \quad [A.6\text{-}2]$$

APPENDIX B: Design and operation of the isoperibolic calorimeter

(excerpted from the manuscript by Dobrogowska and Hepler, in preparation; Smith, 1988.)

The design of the calorimeter is illustrated in Fig. B-1. The calorimeter consists of a glass Dewar vessel (B) (370 cm^3 capacity) suspended and clamped inside a sealed brass can (A). The brass can is fitted with an inlet port through which a liquid can be admitted to the Dewar vessel by an automatic titrator. Changes in the temperature of the mixture in the vessel are monitored with a thermistor (F) and a resistance bridge. A calibration heater (C) mounted on the inside of the lid of the can is position near the bottom of the Dewar vessel. Stirring is provided by means of a glass stirrer (E) which is driven at 720± 2 r.p.m. by a small synchronous motor. More detailed description of the calorimeter is available from Dobrogowska and Hepler (manuscript in preparation).

To begin an experiment the reaction mixture is weighed into the Dewar flask (B). The flask is then clamped to the inside of the brass can (A) as shown in Fig. B-1 and the calorimeter is placed in a constant temperature water bath. The resistance of the thermistor (F) is monitored using a resistance bridge. When the resistance of the thermistor attains a value that has been shown by separate experiments to correspond to the temperature of the water bath, a known volume of titrant is introduced to the Dewar flask from the outlet of the titrant delivery tube (D). The interaction of the titrant with the reaction mixture leads to a change in the temperature of the mixture in the Dewar and a corresponding change in the resistance of the thermistor. The temperature of

the mixture then gradually relaxes back towards the temperature of the surrounding water bath. During this relaxation period the resistance of the thermistor is recorded as a function of time. When the change in resistance of the thermistor with time has been constant for several minutes, the calibration heater is switched on. The voltage across the heater, V_h, and the time of heating, t, are recorded using the circuit shown in Fig. B-2. The current through the heater, I_h, is calculated from the measured voltage across a standard resistor (SR). After the heater has been switched off the resistance of the thermistor as a function of time is again recorded.

A typical plot of the resistance of the thermistor as a function of time for one complete calorimetric experiment is given in Fig. B-3. The solid lines in Fig. B-3 represent the reconstructed calorimetric record that was determined using the method of Vanderzee (1981). The two vertical lines in Fig. B-3 represent the instantaneous changes in resistance of the thermistor due to the titration and the electrical calibration. Since the total heat capacity of the calorimeter is the same for the titration and the electrical calibration, the ratio of the heights of the veritcal lines in Fig. B-3 is equal to the ratio of the energies associated with the two processes. The electrical energy of the calibration is known from $Q_c = I_h V_h t$ and hence the energy associated with the titration can be calculated.

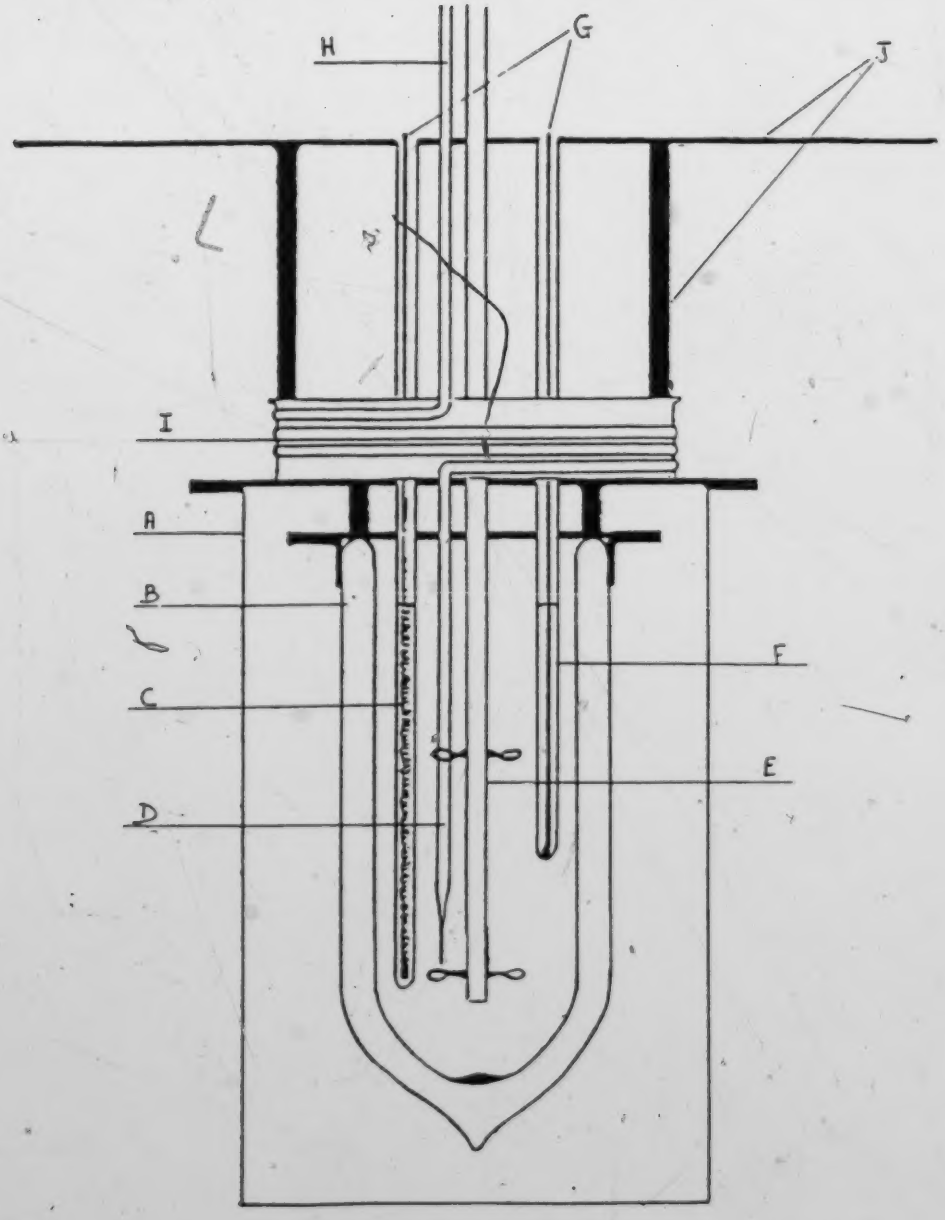
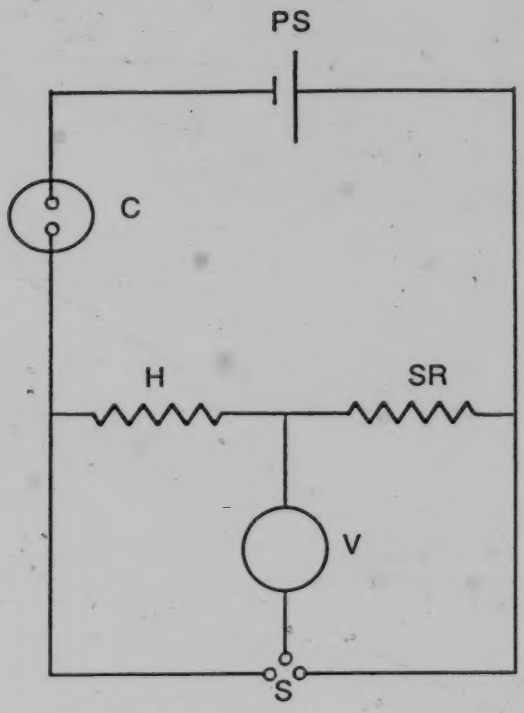


Fig. B-1 Cross-sectional diagram of isoperibol calorimeter (captions on following page)

A	brass can
B	Dewar flask
C	heating element immersed in paraffin oil
D	outlet of titrant delivery tube
E	stirrer
F	thermistor immersed in paraffin oil
G	exit tubes for heater and thermistor lead wires
H	titrant delivery tubing
I	heat exchange coil to bring titrant solution to the temperature of the constant temperature bath surrounding the calorimeter
J	brass lid and supports



PS	power supply
SR	standard resistor, 10.004 Ω
V	voltmeter
H	heater
C	clock
S	switch

Fig. B-2 Diagram of electrical calibration circuit

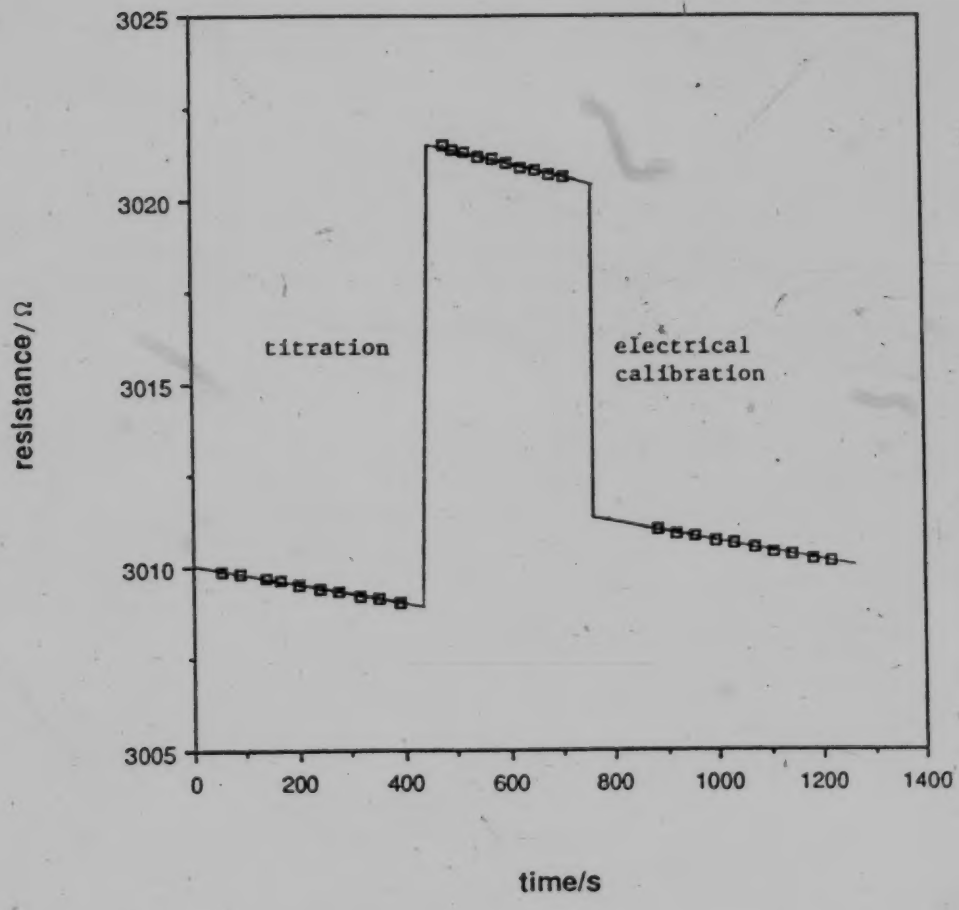


Fig. B-3 Typical plot of the resistance of the thermistor against time. Points are experimental; solid line represents the reconstructed calorimetric record (adapted from Smith, 1988).

APPENDIX C: Calorimetric data for the water-glycerol system at 25°C

Table C-1 Relative partial molar enthalpy of water in water-glycerol system at 25 °C

x_2	$\bar{L}_1$ [J/mol]	x_2	$\bar{L}_1$ [J/mol]
0	0.0	0.3443	-643.2
0.0087	-2.2	0.3517	-671.7
0.0097	-3.8	0.3624	-678.6
0.0110	-4.3	0.3727	-705.9
0.0125	-5.9	0.3790	-725.9
0.0140	-5.2	0.3871	-710.4
0.0153	-6.2	0.3965	-741.6
0.0171	-7.6	0.4483	-779.7
0.0206	-10.0	0.4718	-915.2
0.0216	-9.9	0.4800	-850.8
0.0227	-7.9	0.5034	-893.4
0.0244	-12.4	0.5291	-927.7
0.0251	-14.4	0.5560	-899.3
0.0276	-16.5	0.5825	-1026.2
0.0281	-17.2	0.6028	-1046.8
0.0319	-20.7	0.6309	-1113.0
0.0320	-21.4	0.6692	-1180.1
0.0354	-34.6	0.6721	-1172.3
0.0394	-39.5	0.6846	-1203.3
0.0443	-55.7	0.7006	-1274.4
0.0506	-56.9	0.7175	-1286.4
0.0568	-54.9	0.7351	-1261.3
0.0640	-69.3	0.7515	-1302.9

0.0732	-88.3
0.0842	-126.9
0.0946	-152.0
0.1051	-240.0
0.1155	-214.4
0.1303	-276.0
0.1334	-222.6
0.1452	-249.9
0.1573	-284.9
0.1696	-308.1
0.1817	-366.3
0.1917	-364.5
0.2032	-371.8
0.2242	-418.9
0.2369	-453.5
0.2539	-488.4
0.2773	-533.0
0.2949	-561.4
0.3049	-572.4
0.3215	-597.9
0.3336	-627.7
0.7560	-1747.8
0.7687	-1408.6
0.7798	-1873.6
0.7844	-1292.4
0.7960	-1411.6
0.8030	-1858.2
0.8145	-1572.1
0.8391	-1902.0
0.8630	-1554.8
0.8817	-1851.2
0.9084	-2037.7
0.9084	-2015.6
0.9312	-2638.3
0.9520	-1907.3
0.9675	-2869.7
0.9803	-3519.2
0.9957	-4835.0
0.9966	-4627.4
0.9973	-3961.5
0.9986	-3911.6

Table C-2 Heat of dilution of glycerol

situation: solution in Dewar vessel; pure water in titrator.

Before dilution		H_2O added	After dilution	
m^i	W_s	W_w	m^f	Q
[mol/kg]	[g]	[g]	[mol/kg]	[J]
108584.7	378.66	0.99	4123.8	-157.4
4123.8	379.66	0.99	2062.0	-193.4
2062.0	380.65	0.99	1374.6	-157.7
1374.6	381.65	1.49	916.4	-157.7
916.4	383.15	1.99	634.4	-291.4
634.4	385.14	1.99	485.2	-225.1
485.2	387.13	2.99	358.6	-307.2
358.6	390.13	1.99	305.5	-293.5
305.5	392.12	1.49	274.9	-157.3
274.9	393.62	1.99	242.6	-315.5
242.6	395.61	2.49	211.5	-256.8
211.5	398.10	2.99	183.3	-311.0
183.3	401.09	2.99	161.7	-290.1
267.7	355.84	2.99	223.0	-260.9
223.0	358.83	0.99	210.4	-77.6
210.4	359.83	1.49	194.0	-106.9
194.0	361.33	1.99	175.6	-155.6
175.6	363.32	1.99	160.5	-143.9
160.5	365.31	1.99	147.8	-139.3
147.8	367.30	2.49	134.5	-177.8
134.5	369.79	1.99	125.5	-140.8
125.5	371.78	2.49	115.7	-166.3
115.7	374.27	1.99	109.0	-130.4
125.9	285.41	4.99	103.2	-324.7

103.2	290.40	4.99	87.42	-108.0
87.42	295.39	2.49	81.20	-144.7
81.76	299.05	3.99	73.41	-227.3
73.41	303.04	4.49	65.84	-249.1
65.84	307.53	4.99	59.07	-257.0
59.07	312.52	4.99	53.57	-247.5
53.57	317.51	4.99	49.00	-235.6
51.32	278.71	3.49	47.89	-177.3
47.89	282.20	1.49	46.55	-51.4
46.55	283.70	3.49	43.71	-151.0
43.71	287.18	3.49	41.20	-190.8
41.20	290.67	3.49	38.95	-97.9
37.13	297.34	2.49	35.80	-102.5
35.80	299.83	2.99	34.33	-117.9
34.33	302.82	1.99	33.41	-80.2
33.42	304.82	1.99	32.55	-78.0
32.55	306.81	4.99	30.56	-188.0
30.56	311.80	2.49	29.66	-92.8
29.66	314.29	2.99	28.64	-106.8
28.64	317.28	5.48	26.95	-190.9
27.70	319.94	9.97	24.94	-330.9
24.94	329.91	4.99	23.76	-158.5
23.76	334.90	4.99	22.68	-155.5
22.68	339.88	14.96	19.97	-443.3
19.97	354.84	14.96	17.83	-405.6
18.18	349.86	14.96	16.31	-376.6
16.31	364.82	4.99	15.77	-116.0
15.77	369.80	9.97	14.79	-110.3
14.79	379.77	14.96	13.53	-308.7
13.53	394.73	9.97	12.81	-201.7
12.81	404.70	14.96	11.85	-304.2
11.87	318.75	14.96	10.81	-255.9
10.81	333.71	14.96	9.925	-236.6
9.925	348.66	19.94	8.946	-276.5
8.946	368.60	19.94	8.142	-246.4

8.990	261.62	24.93	7.657	-381.9
7.657	286.54	19.94	6.845	-237.3
6.845	306.48	19.94	6.188	-265.6
6.188	326.43	29.91	5.410	-252.4
5.493	231.13	24.93	4.726	-175.6
4.726	256.05	29.91	4.047	-146.5
4.047	285.96	29.91	3.539	-115.1
3.539	315.9	30.41	3.138	-92.7
3.182	240.50	29.91	2.741	-94.5
2.741	270.41	29.91	2.407	-92.5
2.407	300.32	29.91	2.146	-65.6
2.146	330.23	30.41	1.933	-58.4
1.956	326.87	29.91	1.702	-34.3
1.702	296.96	29.91	1.507	-28.6
1.507	267.05	29.91	1.352	-23.9
1.352	237.14	29.91	1.226	-13.2
1.981	237.15	34.90	1.688	-41.5
1.688	272.05	34.90	1.470	-32.0
1.470	306.95	34.90	1.302	-24.0
1.289	344.86	35.89	1.158	-19.8
1.157	243.74	29.91	1.018	-16.6
1.018	273.65	29.91	0.9096	-12.7
0.9096	303.47	29.91	0.8218	-10.3
0.8218	333.47	29.91	0.7495	-8.7
0.7510	229.98	34.90	0.6593	-11.5
0.6593	259.89	34.90	0.5776	-8.2
0.5776	295.04	35.39	0.5119	-7.4
0.5119	330.44	34.90	0.4603	-4.3

Note: m^i, m^f = initial and final molalities of the solution in Dewar respectively;

W_s = weight of solution in Dewar;

W_w = Weight of water added;

$\overset{\frown}{Q}$ = measured heat.

APPENDIX D: Evaluation of the excess Gibbs energy (molality standard state) from osmotic coefficient data

For a binary system,

$$G = n_1 \mu_1 + n_2 \mu_2$$

$$G^{(m)} = \frac{G}{n_1 M_1} = \frac{\mu_1}{M_1} + m_2 \mu_2 = \left(\frac{\mu_1^{ID}}{M_1} + m_2 \mu_2^{ID}\right) + G^{E(m)}$$

Hence,

$$G^{E(m)} = \frac{(\mu_1 - \mu_1^{ID})}{M_1} + m_2 (\mu_2 - \mu_2^{ID}) = \frac{\mu_1^E}{M_1} + m_2 \mu_2^E$$

Since $x_2/x_1 = m_2 M_1$, if $x_1 \sim 1$, $x_2 \sim M_1 m_2$ and $\ln x_1 \sim - M_1 m_2$.

$$\mu_1^{ID} = \mu_1^{\cdot} + R T \ln x_1 = \mu_1^{\cdot} - R T M_1 m_2$$

$$\begin{aligned} \mu_1^E &= \mu_1 - \mu_1^{ID} \\ &= (\mu_1 - \mu_1^{\cdot}) + R T M_1 m_2 \\ &= R T \ln a_1 + R T M_1 m_2 \end{aligned}$$

Since $\ln a_1 = - M_1 m_2 \phi$, (Lewis and Randall, 1961)

$$\mu_1^E = - R T M_1 m_2 (\phi - 1)$$

$$\mu_2^{ID} = \mu_2^{\circ} + R T \ln \left(\frac{m_2}{m_2^{\circ}}\right)$$

$$\mu_2^E = \mu_2 - \mu_2^{ID}$$

$$= \mu_2 - \mu_2^{\circ} - RT \ln \left(\frac{m_2}{m^{\circ}}\right)$$

$$= RT \ln a_2 - RT \ln \left(\frac{m_2}{m^{\circ}}\right)$$

$$= RT \ln (m_2 \gamma_2) - RT \ln m_2 = RT \ln \gamma_2$$

Therefore,

$$G^{E(m)} = -RT m_2 (\phi - 1) + m_2 (RT \ln \gamma_2)$$

Let $RT(\phi - 1) = a m_2 + 2b m_2^2 + ...$, where a, b, ... are coefficient constants.

$$\ln \gamma_2 = \ln \frac{a_2}{m_2}$$

$$= (\phi - 1) + \int_0^{m_2} \frac{(\phi - 1)}{m_2} dm_2 \qquad \text{(Lewis and Randall, 1961)}$$

$$= \frac{(am_2 + 2bm_2^2 + ...)}{RT} + \frac{1}{RT} \int_0^{m_2} (a + 2bm_2 + ...)\, dm_2$$

$$RT \ln \gamma_2 = 2a m_2 + 3b m_2^2 + ...$$

As a result,

$$G^{E(m)} = a m_2^2 + b m_2^3 + ...$$

In order to find the coefficient constants a, b, ..., plot $(\phi - 1)/m_2$ against m_2 and fit the data point with a polynomial. The osmotic coefficient (ϕ) data can be determined either by freezing point measurement or vapor pressure measurement.

APPENDIX E: Conversion of the excess Gibbs energy from molality standard state to mole fraction standard state

At infinite dilution, $m_i = 55.51\ x_i$, and

$$\frac{a_i^{(x)}}{x_i} = 1 \quad ; \quad \frac{a_i^{(m)}}{m_i} = 1$$

That is,

$$\frac{a_i^{(m)}}{m_i} = \frac{a_i^{(x)}}{x_i}$$

Hence,

$$a_i^{(m)} = a_i^{(x)} \left(\frac{m_i}{x_i}\right) = 55.51\ a_i^{(x)}$$

or

$$m_i\, \gamma_i^{(m)} = 55.51\ x_i\, \gamma_i^{(x)}$$

$$\gamma_i^{(m)} = \frac{55.51\ x_i}{m_i}\, \gamma_i^{(x)}$$

For a binary system,

$$\frac{G^{E(x)}}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

$$\frac{G^{E(m)'}}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2^{(m)}$$

$$= x_1 \ln \gamma_1 + x_2 \ln \left(\frac{55.51\, x_2}{m_2}\, \gamma_2^{(x)} \right)$$

$$= x_1 \ln \gamma_1 + x_2 \ln \gamma_2^{(x)} + x_2 \ln \left(\frac{55.51\, x_2}{m_2} \right)$$

Therefore,

$$\frac{G^{E(m)'}}{RT} = \frac{G^{E(x)}}{RT} + x_2 \ln \left(\frac{55.51\, x_2}{m_2} \right)$$

[Note: $G^{E(m)'} = G^{E(m)} / (m_2 + 55.51)$]

APPENDIX F: Relations between the symmetric and unsymmetric convention of the excess enthalpy and Gibbs energy functions

For a binary system,

$$
\begin{aligned}
H^{E^*} &= n_1 (\overline{H}_1 - H_1^{\cdot L}) + n_2 (\overline{H}_2 - \overline{\overline{H}}_2) \\
&= n_1 (\overline{H}_1 - H_1^{\cdot L}) + n_2 (\overline{H}_2 - \overline{\overline{H}}_2) - n_2 (H_2^{\cdot L} - H_2^{\cdot L}) \\
&= n_1 (\overline{H}_1 - H_1^{\cdot L}) + n_2 (\overline{H}_2 - H_2^{\cdot L}) - n_2 (\overline{\overline{H}}_2 - H_2^{\cdot L}) \\
&= H^E - n_2 (\overline{\overline{H}}_2 - H_2^{\cdot L})
\end{aligned}
$$

For molar quantities,

$$
\begin{aligned}
H^{E^*} &= H^E - x_2 (\overline{\overline{H}}_2 - H_2^{\cdot L}) \\
&= H^E - x_2 \lim_{x_2 \to 0} (H^E)
\end{aligned}
$$

Since

$$
\frac{\gamma_2}{\gamma_2} = \overline{\overline{\gamma}}_2
$$

$$
\begin{aligned}
G^{E^*} &= RT (x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \\
&= RT [x_1 \ln \gamma_1 + x_2 (\ln \gamma_2 - \ln \overline{\overline{\gamma}}_2)] \\
G^{E^*} &= G^E - RT x_2 \ln \overline{\overline{\gamma}}_2
\end{aligned}
$$

APPENDIX G: Sensitivity tests on UNIQUAC parameters

Because of the complexity of the UNIQUAC expression, the effect of an individual parameter on excess functions is not obvious. One simple and straightforward method to test the sensitivity of a parameter is by noting the change of the function value as any particular parameter is changed while keeping other parameters constant. In this study, the effects of individual UNIQUAC parameter on excess entropy and excess enthalpy have been investigated.

The UNIQUAC expression for excess entropy (equation [4.1-6]) depends on the r, q, a_{12} and a_{21} parameters (for a binary system). Fig. G-1 illustrates the effect on the excess entropy of the water-ethylene glycol system by reducing each of the four parameters (r_2, q_2, a_{12} and a_{21}) individually (i.e., reduce one at a time; the rest are kept the same as the reference values) to half the value of the reference parameter concerned; similarly, Fig. G-2 shows the effect by adding half the value of the reference parameter to each parameter concerned. The curve S(ref) in Fig. G-1 and G-2 stands for the reference entropy curve which is calculated by using the literature values of r, q, a_{12} and a_{21} (Nath and Bender, 1983; at 65.1°C). Curve1 of Fig. G-1 shows the effect by reducing r_2 to half of the reference value while keeping other parameters same as the reference values; curve1 of Fig. G-2 indicates the effect by adding half the r_2 value to the original reference value. In the same way, curve2 is for q_2, curve3 is for a_{12} and curve4 is for a_{21}. Both Fig. G-1 and G-2 show that the change of either r_2 or q_2 have relatively greater effect on the resulting excess entropy value as compared to the effect by a_{12} or a_{21}.

The UNIQUAC expression for excess enthalpy (equation [4.1-5]) is determined by q and the energy parameters. Fig. G-3 and G-4 show the effect of changing q_2, a_{12} or a_{21} individually on the excess enthalpy of the water-ethylene glycol system. Apparently, a_{21} has the greatest influence on the enthalpic function. However, it is difficult to compare the effect of a_{12} and q_2. Thus instead, we re-calculate the excess enthalpy by changing (reducing or adding 50% of the reference values) the energy parameters, a_{12} and a_{21}, simultaneously and then compare the effect caused by changing q_2 alone. These are illustrated in Fig. G-5 and G-6. From Fig. G-5 and G-6, we may conclude that the energy parameters are the controlling parameters for the excess enthalpy function.

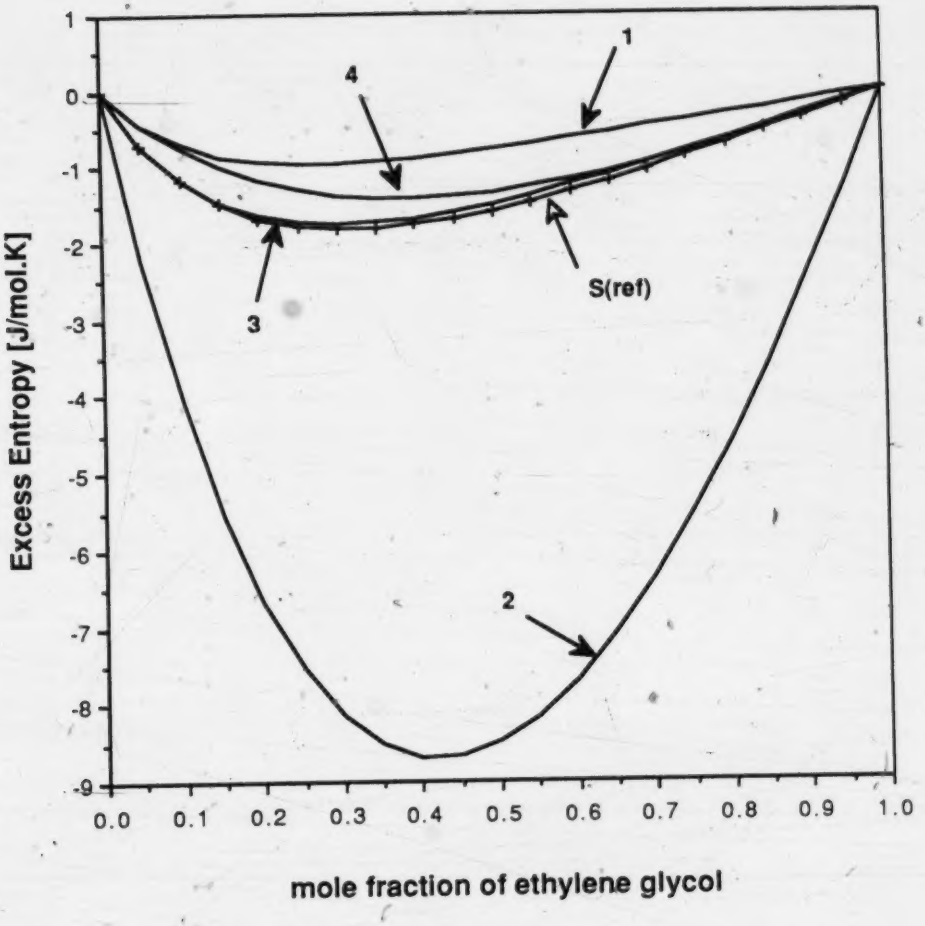


Fig. G-1 Effect of reduced r_2 , q_2, a_{12} and a_{21} on excess entropy. Curve S(ref) is the reference entropy curve calculated from literature values reported by Nath and Bender (1983).
curve1: $r_2 = 0.5\ r_2(ref)$; curve2: $q_2 = 0.5\ q_2(ref)$
curve3: $a_{12} = 0.5\ a_{12}(ref)$; curve4: $a_{21} = 0.5\ a_{21}(ref)$

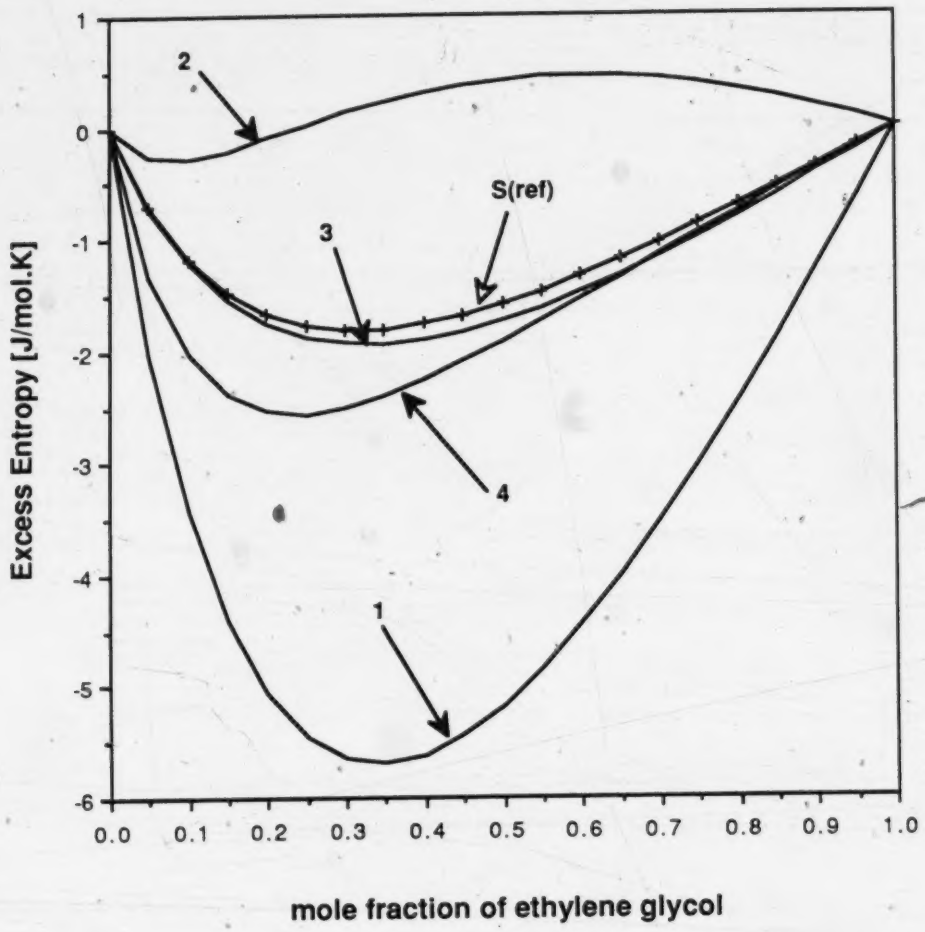


Fig. G-2 Effect of increased r_2 , q_2, a_{12} and a_{21} on excess entropy. Curve S(ref) is the reference entropy curve calculated from literature values reported by Nath and Bender (1983).
curve1: $r_2 = 1.5\ r_2(ref)$; curve2: $q_2 = 1.5\ q_2(ref)$
curve3: $a_{12} = 1.5\ a_{12}(ref)$; curve4: $a_{21} = 1.5\ a_{21}(ref)$

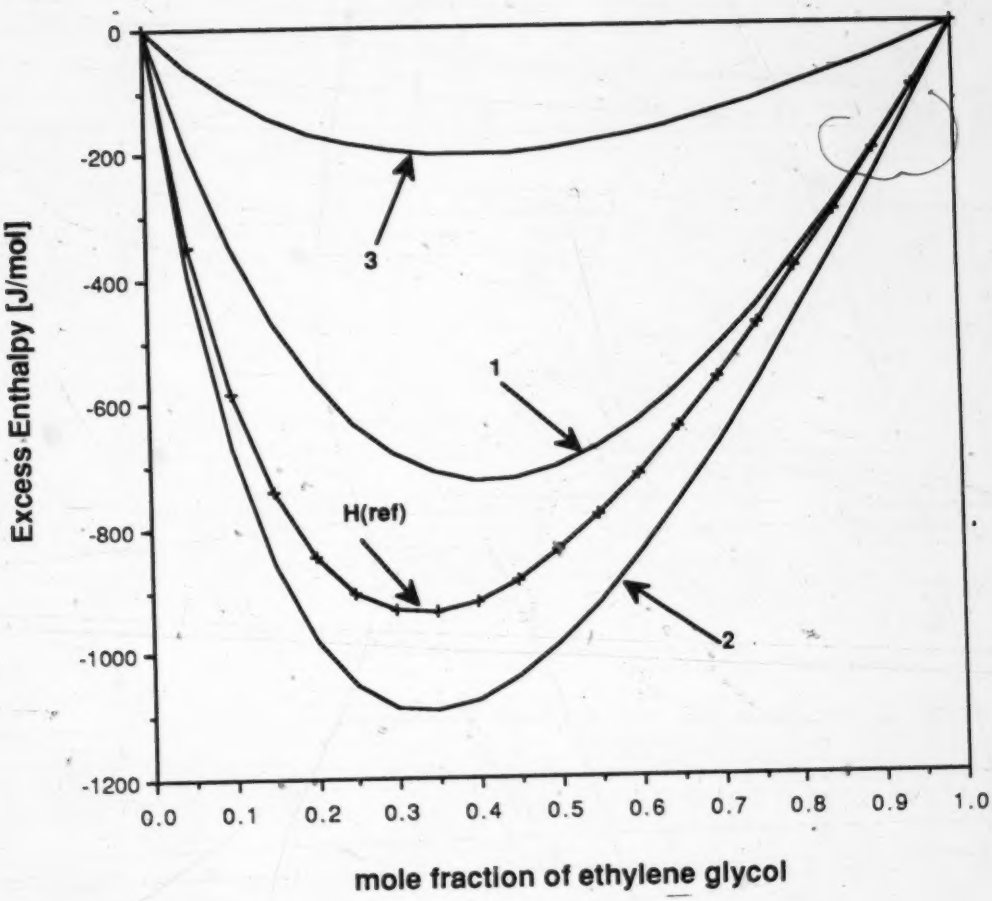


Fig. G-3 Effect of reduced q_2, a_{12} and a_{21} on excess enthalpy.
Curve H(ref) is the reference enthalpy curve calculated from literature values reported by Nath and Bender (1983).
curve1: $q_2 = 0.5\ q_2(ref)$;curve2: $a_{12} = 0.5\ a_{12}(ref)$
curve3: $a_{21} = 0.5\ a_{21}(ref)$

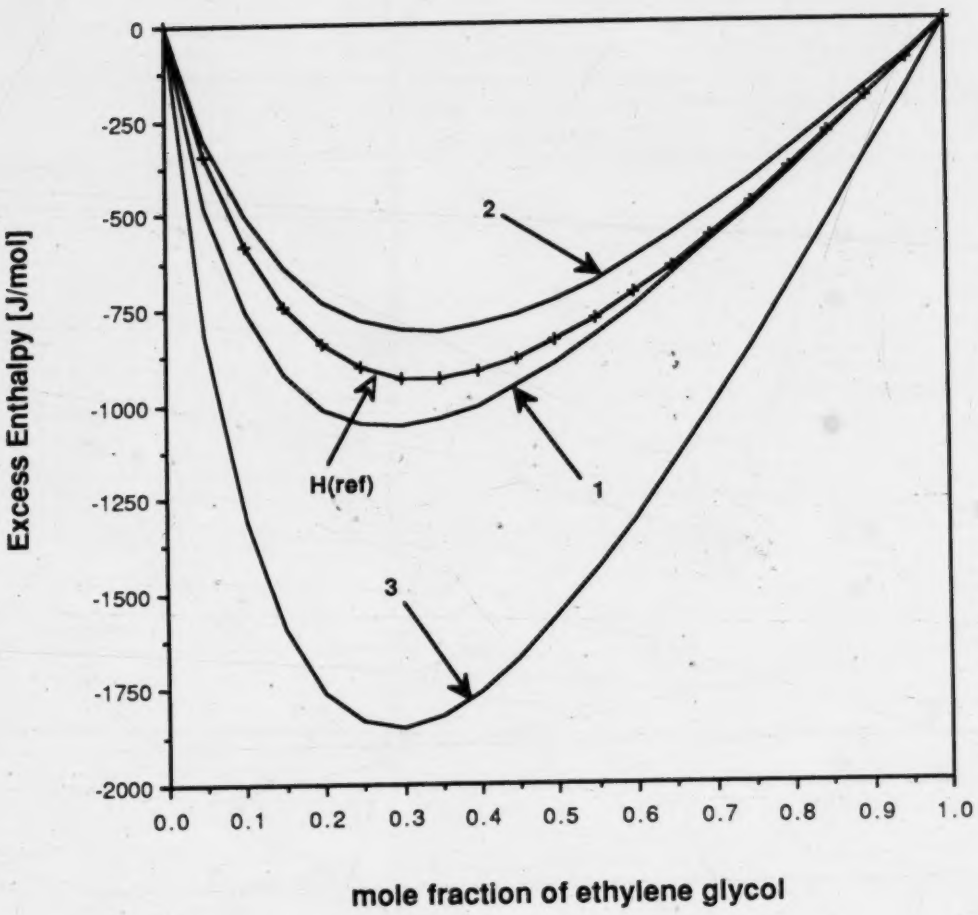


Fig. G-4 Effect of increased q_2, a_{12} and a_{21} on excess enthalpy. Curve H(ref) is the reference enthalpy curve calculated from literature values reported by Nath and Bender (1983).
curve1: $q_2 = 1.5\ q_2(ref)$;curve2: $a_{12} = 1.5\ a_{12}(ref)$
curve3: $a_{21} = 1.5\ a_{21}(ref)$

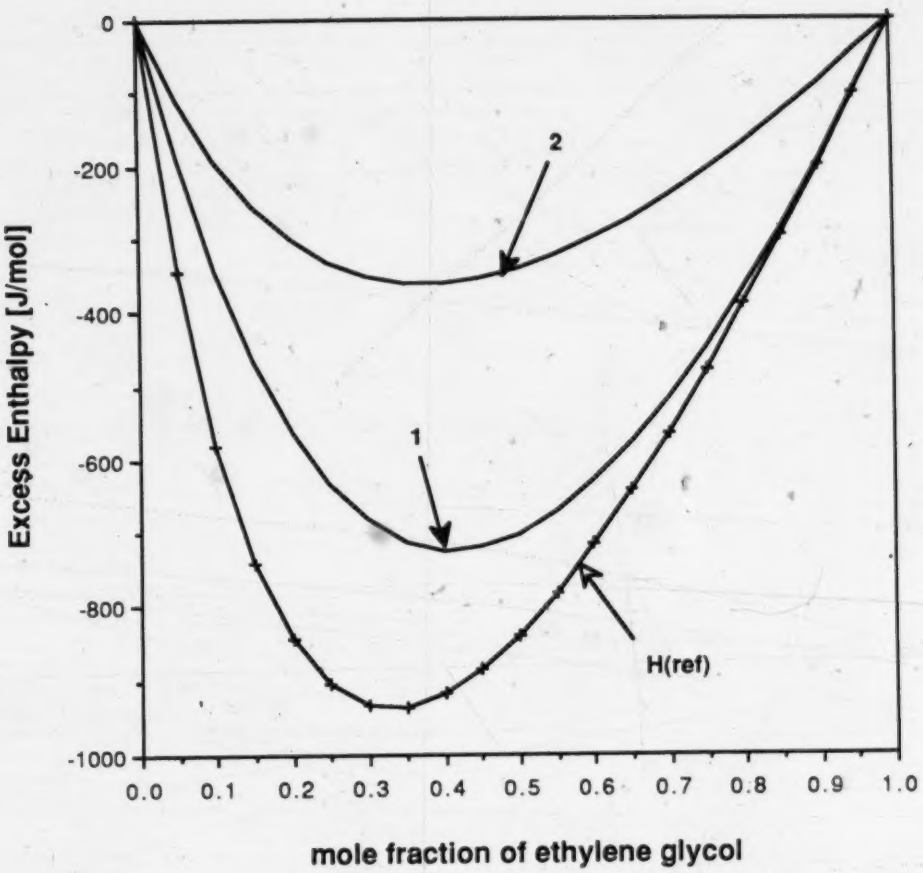


Fig. G-5 Effect of reduced q_2 and the energy parameters on excess enthalpy. Curve H(ref) is the reference enthalpy curve calculated from literature values reported by Nath and Bender (1983).
curve1: $q_2 = 0.5\ q_2(\text{ref})$
curve2: $a_{12} = 0.5\ a_{12}(\text{ref})$ and $a_{21} = 0.5\ a_{21}$ (ref).

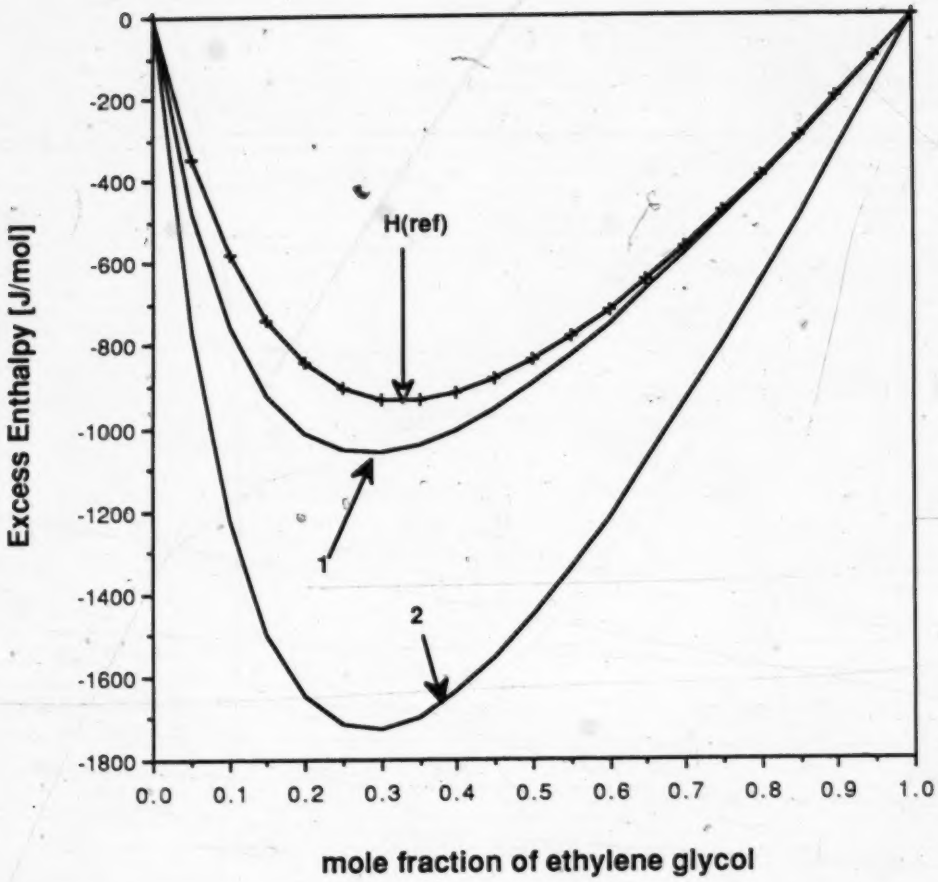


Fig. G-6 Effect of increased q_2 and the energy parameters on excess enthalpy. Curve H(ref) is the reference enthalpy curve calculated from literature values reported by Nath and Bender (1983).
curve1: $q_2 = 1.5\ q_2(\text{ref})$
curve2: $a_{12} = 1.5\ a_{12}(\text{ref})$ and $a_{21} = 1.5\ a_{21}$ (ref).